

Rheological Properties of Telechelic Associative Polymer in Aqueous Solution

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Chapter 1: Introduction

1-1. Background

Polymers exhibit various structures due to their chain-like flexible backbones, and they exhibit very complicated dynamics which cannot be observed for low-molecular weight systems¹⁻³. When polymers are dissolved in solvents and the polymer concentrations are not large, polymer solutions essentially behave as viscous fluids (although their rheological properties are not so simple). However, if polymer chains in solutions are cross-linked each other to form network structures (gels), the mechanical properties qualitatively change. Such gels can behave as elastic solids, unlike simple polymer solutions⁴.

The structures and dynamics of gels have been studied extensively⁴. In general, gels can be categorized into two classes; the chemical gels and the physical gels. In the chemical gels, polymer chains are connected by covalent bonds as shown in Figure 1-1. Because the covalent bonds cannot be broken (unless very strong force is applied), the connectivity of a chemical gel does not change with time. The covalent bonds can be interpreted as permanent links. On the other hand, in the physical gels, polymer chains are connected by secondary bonds such as hydrogen bonds, coordination bonds, and hydrophobic associations as shown in Figure 1-2. All of these links can be broken by the thermal fluctuation, and thus they are transient links. In other words, the links in a physical gel have the life time, and the gel network can be dynamically reconnected. Thus the connectivity is no longer permanent.

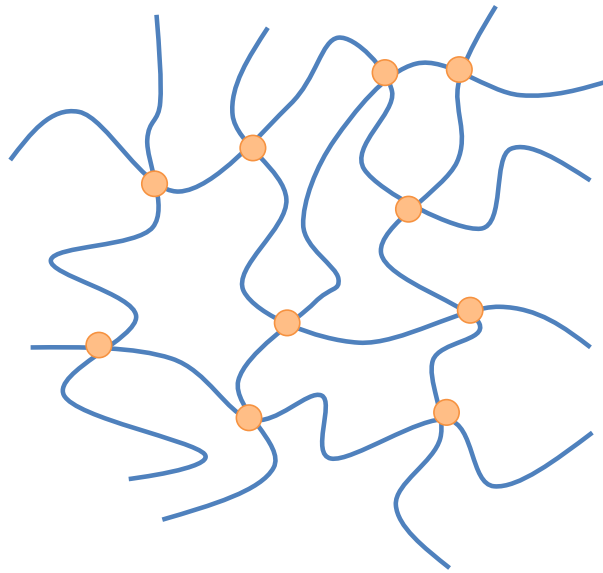


Figure1-1. Schematic illustration of a chemical gel. The polymer chains are connected by covalent bonds. The circles represent the cross-linking via covalent bonds.

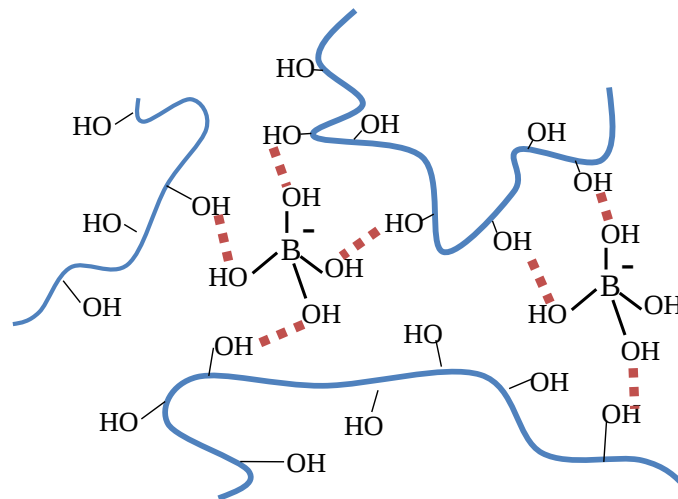


Figure 1-2. Schematic illustration of the slime network as a model physically cross-linked gel. The hydroxide groups of poly vinyl alcohol chain and borate ions are connected via hydrogen bonds.

Physical gels behave as elastic solids at short time scale, just like the chemical gels, but they behave as viscous fluids at long time scale after the reorganization of networks. Therefore, rheologically, the physical gels can be defined as viscoelastic fluids. A well-known and simple

example of a physical gel is the so-called slime, which is the polyvinyl alcohol aqueous solution with borax. In slime, polymer chains and borate ions are connected by hydrogen bonding, as shown in Figure 1-2.

Another simple example is telechelic associative polymer solutions. Telechelic associative polymers have hydrophobic end groups, and the main chains are hydrophilic as shown in Figure 1-3. When dissolved in water, telechelic associative polymers can form micellar structures as illustrated in Figure 1-4. If the polymer concentration is very low (lower than the critical micellar concentration, CMC), polymer chains are isolated. If the polymer concentration is increased and the concentration becomes above the CMC, telechelic associative polymers form micellar structure. Because telechelic associative polymers have long main chain, the formed micellar structures are expected to have a characteristic flower like shape and are often referred to as “flower micelles”. If the concentration is increased further, flower micelles overlap with each other, and some flower micelles can be connected by “bridge” chains. The network can span all the solutions, if the bridge chain fraction is sufficiently high. Thus the telechelic associative polymer solutions become physical gels^{4,5}.

Hydrophobically modified ethoxylated urethane (HEUR) is one of the most popular telechelic associative polymers. HEUR has a polyethylene oxide (PEO) main chain and hydrophobic chain end groups such as alkyl chains. The PEO main chain and end groups are connected by urethane bonds. (The details of the chemical structures and synthesis method will be given in Chapter 2.) Due to their simple structures, HEUR can be utilized as a model telechelic associative polymer to

study structures and dynamics⁵⁻¹². It would be worth mentioning here that because HEUR is water-soluble and HEUR solutions have high viscosity, they are widely utilized as thickeners for various industrial purposes. The scientific knowledge on HEUR will be informative to control the properties of thickeners.

So far, various studies have been done to clarify the structures and dynamics of HEUR solutions³⁻³⁵. Despite extensive studies, however, the structures and dynamics of HEUR aqueous solutions are not fully understood. In this thesis, the rheological properties of HEUR aqueous solutions are studied in detail.

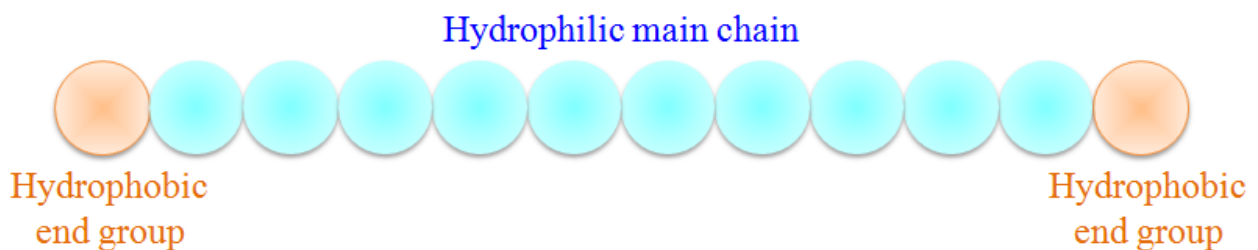


Figure 1-3. Schematic illustration of a telechelic associative polymer chain.

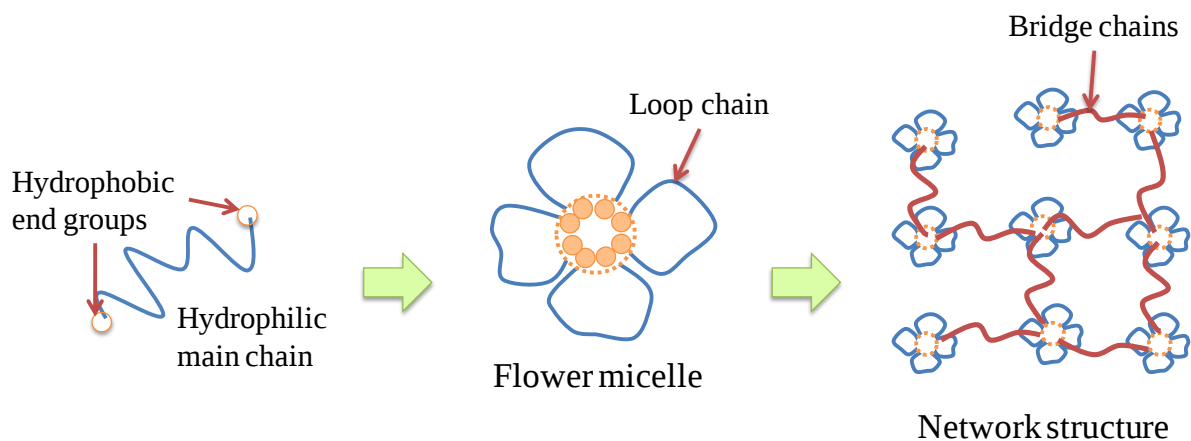


Figure 1-4. Schematic illustrations of telechelic associative polymer structures. When the polymer concentration is well below the critical micellar concentration, CMC, telechelic polymer exhibits the isolated single chain conformation. When the polymer concentration is above CMC, flower micelles can form. As the polymer concentration further increases, flower micelles are connected by the bridge chains.

1-2. Rheology of Hydrophobically Modified Ethoxylated Urethane

1-2-1. Linear Viscoelasticity

Mechanical measurements have been extensively conducted to investigate the rheological properties of HEUR solutions³⁻¹². The experimental data by Tam et al⁶ for the 2wt% HEUR aqueous solution clearly showed that the linear viscoelasticity of HEUR aqueous solutions can be well described by single Maxwell type relaxation. Namely, the shear relaxation modulus can be expressed as

$$G(t) = G_0 e^{-t/\tau} \quad (1-1)$$

and equivalently, the storage and loss moduli can be expressed as

$$G'(\omega) = G_0 \frac{(\tau\omega)^2}{1 + (\tau\omega)^2}, \quad G''(\omega) = G_0 \frac{\tau\omega}{1 + (\tau\omega)^2} \quad (1-2)$$

where G_0 and τ being the characteristic modulus and the relaxation time, respectively. The single Maxwell type relaxation has been observed for many other HEUR aqueous solutions with relatively low concentrations and can be considered as one of characteristic properties of those solutions. The single Maxwell type relaxation suggests that the HEUR network has one relaxation time scale in the terminal regime. (As shown below, such a simple relaxation process can be well reproduced by a mean-field single-chain model³⁶⁻³⁸.)

Nevertheless, some experimental studies revealed non-single Maxwell type relaxation of concentrated HEUR aqueous solutions. For example, Annable et al⁵ reported that a 7wt% HEUR aqueous solution exhibits deviation from the single Maxwell type. Currently, the origin of this deviation is not yet clear. Annable et al⁵ also showed that the characteristic modulus and the

relaxation time depend on the HEUR concentration rather strongly. Such strong dependence cannot be explained by a simple single-chain model³⁶⁻³⁸.

1-2-2. Nonlinear Viscoelasticity

HEUR aqueous solutions are also extensively studied for their nonlinear rheological properties^{5,6,13-35}. One characteristic nonlinear behavior of HEUR aqueous solutions is the shear thickening. In a certain range of shear rates, the shear viscosity of the HEUR solution increases with increasing shear rate. This is in contrast to polymer solutions and melts that usually exhibit monotonic thinning (monotonic decreases of the shear viscosity with the rates¹⁻³). The shear thickening behavior of HEUR aqueous solutions can be observed at relatively low shear rates, and the shear thinning behavior prevails at higher rates. Such complex shear rate dependence cannot be expected from the simple linear viscoelasticity, and the origins of the shear thickening and thinning in HEUR aqueous solutions are still controversial. Some researchers claim that the shear thickening is caused by the increase of the number density of bridge chains that sustain the shear stress, and the others claim that it is due to the nonlinear elasticity of stretched HEUR chains³⁹⁻⁵⁰. In addition, the shear thinning has been attributed to the decrease of bridge chain density due to extraction under flow³⁹⁻⁵⁰.

Pellens et al²⁸ measured the shear rate dependence of the shear viscosity and first normal stress coefficient for the 2.9wt% HEUR solution. Their data, showing weak shear thickening of the shear viscosity and slight thinning of the first normal stress coefficient (Figure 1-5), cannot be explained

by simple mechanisms mentioned above. Recently, observation of the shear flow field has become possible. Berret et al²³ measured the flow field in a 3wt% HEUR aqueous solution under steady shear and reported that the flow field is not uniform, as shown in Figure 1-6. For this case, the macroscopic mechanical responses (including the thinning and thickening) measured by usual rheometers are just apparent. Then, detailed and systematic analysis will be required to clarify the thickening and thinning mechanisms in HEUR aqueous solutions.

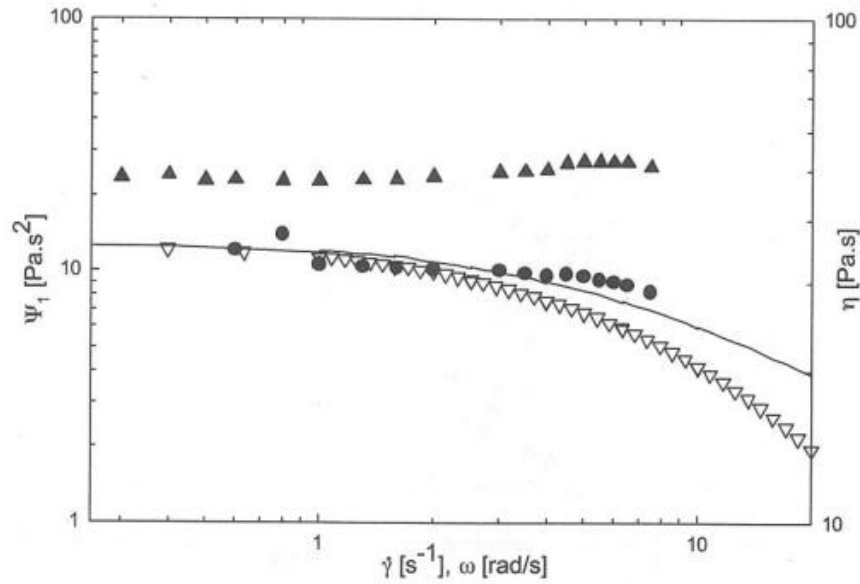


Fig.1-5 Steady shear viscosity(▲), first normal stress coefficient(●), and $2G'(\omega)/\omega^2$ (▽) of 2.9wt% HEUR ($M_w=20k$) aqueous solution at 20°C ²⁸. The HEUR chain has hydrophobic hexadecyl groups at its ends.

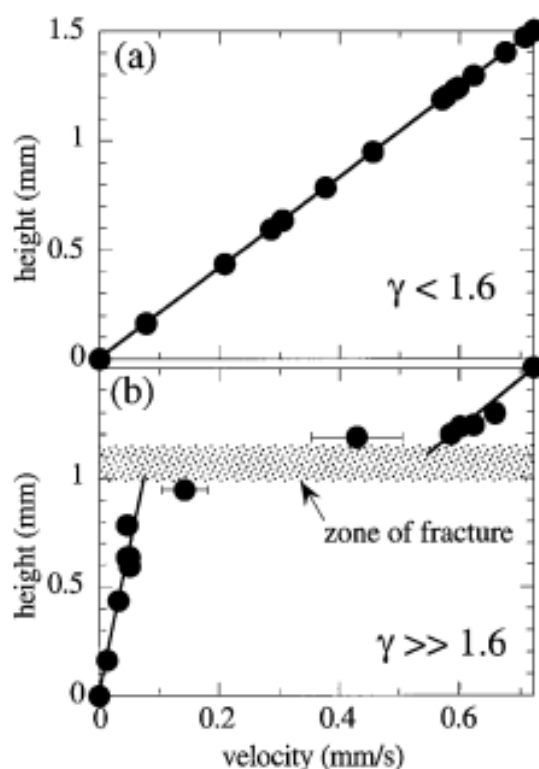


Figure 1-6. Velocity profiles of 3.0 wt% HEUR aqueous solution for (a) $\gamma < 1.6$ and (b) $\gamma \gg 1.6$, respectively²³. The (apparent) shear rate was 0.45 s^{-1} , and the profiles (a) and (b) were obtained at short and long times after the start-up of flow and after long time, respectively. At large strain (long time), the non-uniform shear flow was observed.

1-3. Transient Network Models

Many theoretical studies have been made in attempt of explaining the rheological properties of telechelic associative polymer solutions. Among many models, the so-called transient network model³⁶⁻³⁸ appears to be promising. This model is a mean-field single-chain model, in which the dynamics of a tagged chain is considered. Because the life time of the hydrophobic association is finite, a bridge chain can be detached from a micellar core to become a dangling chain. Conversely, a dangling chain can attach to a micellar core to become a bridge chain.

Based on such a physical picture as illustrated in Figure 1-7, the transient network model assumes that a tagged polymer chain can take two different states; bridge and dangling states. If the probability distributions of the bridge and dangling states having the end-to-end vector $\mathbf{r}$ are expressed as $\psi(\mathbf{r},t)$ and $\phi(\mathbf{r},t)$, respectively, the dynamics of the system can be described by the time-evolution equations for $\psi(\mathbf{r},t)$ and $\phi(\mathbf{r},t)$. Under the mean-field approximation, these equations can be expressed as

$$\frac{\partial \psi(\mathbf{r},t)}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot [\boldsymbol{\kappa} \phi(\mathbf{r},t)] - \beta(\mathbf{r})\psi(\mathbf{r},t) + \alpha(\mathbf{r})\psi(\mathbf{r},t) \quad (1-4)$$

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot [\boldsymbol{\kappa} \phi(\mathbf{r},t)] - \alpha(\mathbf{r})\phi(\mathbf{r},t) + \beta(\mathbf{r})\psi(\mathbf{r},t) \quad (1-5)$$

where $\boldsymbol{\kappa}$ is the velocity gradient tensor, and $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are the dangling-to-bridge and bridge-to-dangling transition rates. The stress tensor $\boldsymbol{\sigma}$ is expressed as

$$\boldsymbol{\sigma} = \nu \int d\mathbf{r} \frac{du(\mathbf{r})}{d\mathbf{r}} \mathbf{r} \psi(\mathbf{r},t) \quad (1-6)$$

Here ν is the spatially averaged number density of the chains, and $u(\mathbf{r})$ is the bond potential determined by the end-to-end vector $\mathbf{r}$.

Both linear and nonlinear viscoelastic properties can be calculated from eqs (1-4)-(1-6). As clearly observed in eqs (1-4)-(1-6), the rheological properties depend on the $\mathbf{r}$ -dependence of $\alpha(\mathbf{r})$, $\beta(\mathbf{r})$, and $u(\mathbf{r})$. Various forms of $\alpha(\mathbf{r})$, $\beta(\mathbf{r})$, and $u(\mathbf{r})$ have been proposed to reproduce the experimentally observed shear thickening and thinning behavior. For example, the “stretch-dependent dissociation rate” model tuning the function $\beta(\mathbf{r})$ and the “elastic potential” model considering the finite extensibility effect and tuning the function $u(\mathbf{r})$ have been proposed³⁸. Although some elaborated models³⁹⁻⁴⁸ can reproduce both the linear and nonlinear viscoelasticity, it

is not so clear whether the fine-tuning of functions $\alpha(\mathbf{r})$, $\beta(\mathbf{r})$, and $u(\mathbf{r})$ is physically reasonable or not.

As explained in Section 1-2, a single model cannot explain all the experimental data . Although the current transient network type models may be a useful theoretical tool to analyze the viscoelasticity of associative polymer solutions, further improvement for the theoretical models is clearly needed. There may be many effects which are overlooked in the current transient network type models.

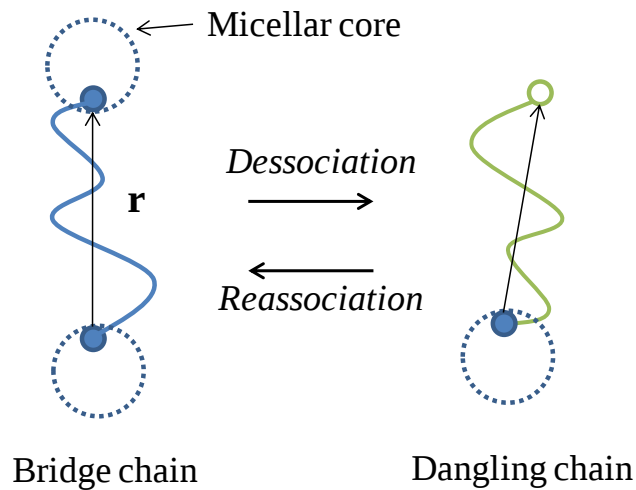


Figure 1-7. Schematic illustrations of structural changes between bridge and dangling chain due to thermal motion.

1-4 Scope of This Thesis

On the basis of the experimental and theoretical studies explained in the previous sections, this thesis attempts to clarify the mechanisms of some rheological properties of model HEUR aqueous solutions. The thesis is constructed as follows.

Chapter 2 shows the material used in this work. The detailed synthesis method and characteristics of HEUR are shown. Furthermore, the principle and method are described for viscoelastic and fluorescent measurements.

In Chapter 3, the shear thickening behavior of a 1wt% HEUR aqueous solution is studied in detail. The experimental data demonstrate that the shear viscosity and the first normal stress difference show different shear rate dependence. To explain this result, a new transient network type model considering an anisotropic bridge formation is proposed.

In Chapter 4, the concentration dependence of the linear viscoelasticity of HEUR aqueous solutions is studied. The concentration dependence of the HEUR solution qualitatively changes at the crossover concentration ($\cong 4\text{wt}\%$). The explanation based on the sparseness of the HEUR network is proposed.

In Chapter 5, the nonlinear viscoelasticity is examined for the HEUR solutions utilized in Chapter 4. The theoretical model incorporating the sparseness of the network predicts that the shear thickening and thinning features also change at the crossover concentration, $\cong 4\text{wt}\%$. The experimental data indeed demonstrate that the thickening of the shear viscosity disappears at the crossover concentration.

In Chapter 6, the mechanisms of the shear thinning is studied with the aid of the fluorescent measurement. The fluorescence data show that the association number of micelles is not sensitive to the shear rate even in the shear thinning region, suggesting that the shear thinning is caused by the decrease of the number density of the elastically active bridge chains.

Finally, Chapter 7 summarizes the experimental results and theoretical analyses for the HEUR aqueous solutions.

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Chapter 2: Samples and Measurements

For full rheological characterization and optical (fluorescent) measurements, HEUR samples having hexadecane groups and/or fluorescent pyrenyl groups at the chain ends were synthesized. This chapter summarizes the method of synthesis and results of molecular characterization of those samples as well as the principles and methods of rheological and optical measurements.

2-1. Synthesis and Characterization of HEUR samples

Hydrophobically-modified ethoxylated urethane (HEUR) samples having hexadecyl groups and/or fluorescent pyrenyl groups at the chain ends were synthesized with a conventional method explained below¹. The structures of these HEUR samples are illustrated in Figures 2-1 and 2-2.

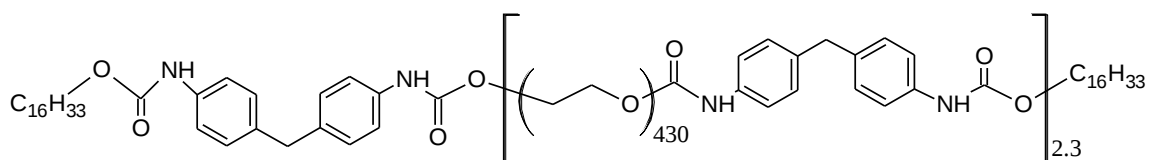


Figure 2-1. Structure of HEUR chain having hexadecyl groups at both ends.

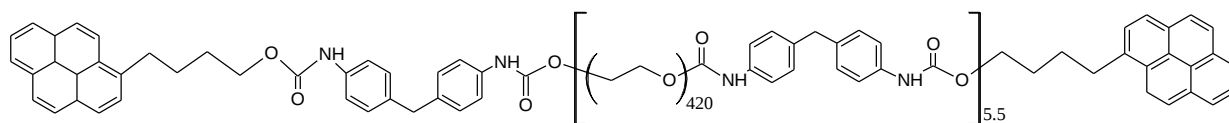


Figure 2-2. Structure of HEUR chain having pyrenyl groups at both ends.

The chemicals utilized in the synthesis, poly(ethylene oxide) (PEO; $M_w = 1.9 \times 10^4$, $M_w/M_n = 1.1$), methylene diphenyl-4,4-diisocyanate (MDPDI), and hexadecanole (HDOH) were purchased from Wako Pure Chemical Industries Ltd, and 1-pyrenyl butanol (Py-BuOH), from Sigma-Aldrich Co. All these chemicals were used without further purification.

The synthesis was conducted in dehydrated tetrahydrofuran (THF; Guaranteed grade, Wako) containing 25wt% of PEO and given masses of MDPDI and end-modifying alcohol, HDOH or Py-BuOH. The molar ratio of these reactants was set as PEO:MDPDI:alcohol = 3:4:2. The PEO chains were first extended through the condensation reaction with MDPDI at 60°C for 2h, and then the end-capping reaction between alcohol and MDPDI, the latter remaining active at the ends of the extended PEO chains, was conducted at 60°C for 24 h. Finally, the reaction mixture was cooled to room temperature, diluted with excess THF, and poured into a large volume of THF/hexane mixture of 1/3 (wt/wt) composition to recover the HEUR sample as a precipitant. The sample was thoroughly dried in a vacuum oven at 40°C.

The HEUR samples thus obtained were characterized with size-exclusion chromatography utilizing a column/pump system (HLC-8320 GPC EcoSEC, Tosoh) equipped with a refractive index monitor. The elution solvent was THF, and commercially available monodisperse PEO samples (Tosoh) were utilized as the elution standards. The weight-average molecular weight and polydispersity index of the HEUR samples, determined from the elution volume calibration with those standards, are summarized in Table 2-1.

Table 2-1. Characteristics of HEUR samples.

sample	$10^{-5}M_w$	M_w/M_n
end-hexadecyl HEUR	0.46	1.35
end-pyrenyl HEUR	1.1	1.78

The HEUR sample having the hexadecyl groups at the chain ends was utilized for full rheological characterization of the HEUR aqueous solutions in Chapters 3-5, and the other HEUR sample having the pyrenyl groups at the ends, for fluorescent tests in Chapter 6.

2-2. Rheological measurements

2-2-1. Principle²

Needless to say, materials subjected to external deformation exhibit mechanical stress. This stress reflects a change(s) in the structure in the material due to the deformation as well as hydrodynamic interaction between the structures/molecules therein. Specifically, for polymeric solutions (the target of this thesis), the structure refers to the conformation of polymeric molecules and associated higher order structure, if any.² Correspondingly, the relaxation of the stress having a non-zero characteristic time(s) represents thermal recovery of the structure, either the polymer conformation or the connectivity of their associated structure.

The materials exhibit either linear or nonlinear viscoelastic responses against the externally applied deformation. The linear response is observed when the deformation is sufficiently small and slow thereby negligibly affecting the thermal, equilibrium dynamics of the structure therein. For this case, all rheological responses of incompressible materials (including the HEUR solutions examined in this thesis study) are characterized by a single material function, the linear relaxation modulus, $G(t)$. $G(t)$ is defined for a material being subjected to an instantaneous small shear strain γ and exhibiting relaxation of the shear stress $\sigma(t)$: $G(t) \equiv \sigma(t)/\gamma$. For arbitrary strain $\gamma(t)$ in the

linear viscoelastic regime, the shear stress of the material is expressed in a convolution form (often referred to as the Boltzmann superposition form),

$$\sigma(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad \text{with} \quad \dot{\gamma}(t') = \frac{d\gamma(t')}{dt'} \quad (2-1)$$

Equation (2-1) serves as a platform relating all linear viscoelastic properties (defined for different types of strain evolution) with the linear relaxation modulus $G(t)$. First of all, $G(t)$ is defined with respect to eq (2-1) for $\gamma(t') = \gamma u(t')$ with $u(t')$ being the Heviside's step function of t' . Furthermore, eq (2-1) defines the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, for a sinusoidal strain as

$$\sigma(t) = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t] \quad \text{for} \quad \gamma(t) = \gamma_0 \sin \omega t \quad (2-2)$$

with

$$G'(\omega) = \omega \int_0^\infty G(t) \sin \omega t dt, \quad G''(\omega) = \omega \int_0^\infty G(t) \cos \omega t dt \quad (2-3)$$

The viscosity growth function $\eta^+(t)$ on start-up of flow at a constant rate $\dot{\gamma}$ at $t > 0$ and the viscosity decay function $\eta^-(t)$ on cessation of steady flow at $t > 0$ are also defined through eq (2-1):

$$\eta^+(t) = \frac{\sigma(t)}{\dot{\gamma}} = \int_0^t G(t') dt' \quad (t > 0) \quad \text{for} \quad \dot{\gamma}(t) = \dot{\gamma} u(t) \quad (2-4)$$

and

$$\eta^-(t) = \frac{\sigma(t)}{\dot{\gamma}} = \int_t^\infty G(t') dt' \quad (t > 0) \quad \text{for} \quad \dot{\gamma}(t) = \dot{\gamma} \{1 - u(t)\} \quad (2-5)$$

The first normal stress difference growth and decay functions $\Psi_1^+(t)$ and $\Psi_1^-(t)$ defined within the framework of quasi-linear responses for the evolution of the first normal stress difference $N_1(t)$ on start-up and cessation of flow are also related to $G(t)$ as well:

$$\Psi_1^+(t) = \frac{N_1(t)}{\dot{\gamma}^2} = 2 \int_0^t t' G(t') dt' \quad (t > 0) \quad \text{for } \dot{\gamma}(t) = \dot{\gamma} u(t) \quad (2-6)$$

and

$$\Psi_1^-(t) = \frac{N_1(t)}{\dot{\gamma}^2} = 2 \int_t^\infty t' G(t') dt' \quad (t > 0) \quad \text{for } \dot{\gamma}(t) = \dot{\gamma} \{1 - u(t)\} \quad (2-7)$$

From eqs (2-4) and (2-6), the steady state values $\eta^+(\infty)$ and $\Psi_1^+(\infty)$ are unequivocally related to the zero-shear viscosity η_0 and steady state recoverable compliance J_e as

$$\eta^+(0) = \eta_0 \quad \text{and} \quad \Psi_{1,0} \equiv \Psi_1^+(\infty) = 2J_e \eta_0^2 \quad (2-8)$$

with

$$\eta_0 = \int_0^\infty G(t) dt \quad \text{and} \quad J_e = \frac{\int_0^\infty t G(t) dt}{\left\{ \int_0^\infty G(t) dt \right\}^2} \quad (2-9)$$

All these linear viscoelastic relations are deduced from eq (2-1) and its extension to the quasi-linear framework (for the second-order fluids).²

In contrast, the equilibrium dynamics and structure are largely affected by large and fast deformation. For this case, the materials exhibit nonlinear viscoelastic responses, and eq (2-1) and its extension to the quasi-linear framework never work. Thus, in this nonlinear regime, there is no unique relation among the viscoelastic properties defined for different types of strain evolution. Nevertheless, the material responses in the nonlinear regime are still characterized with the properties measured in the same way as in the linear regime:

Nonlinear viscosity growth function:

$$\eta^+(t; \dot{\gamma}) = \frac{\sigma(t; \dot{\gamma})}{\dot{\gamma}} \quad (t > 0) \quad \text{for } \dot{\gamma}(t) = \dot{\gamma} u(t) \quad (2-10)$$

Nonlinear viscosity decay function:

$$\eta^-(t; \dot{\gamma}) = \frac{\sigma(t; \dot{\gamma})}{\dot{\gamma}} \quad (t > 0) \text{ for } \dot{\gamma}(t) = \dot{\gamma}\{1 - u(t)\} \quad (2-11)$$

Nonlinear first normal stress difference growth function

$$\Psi_1^+(t; \dot{\gamma}) = \frac{N_1(t; \dot{\gamma})}{\dot{\gamma}^2} \quad (t > 0) \text{ for } \dot{\gamma}(t) = \dot{\gamma}u(t) \quad (2-12)$$

Nonlinear first normal stress difference decay function

$$\Psi_1^-(t; \dot{\gamma}) = \frac{N_1(t; \dot{\gamma})}{\dot{\gamma}^2} \quad (t > 0) \text{ for } \dot{\gamma}(t) = \dot{\gamma}\{1 - u(t)\} \quad (2-13)$$

2-2-2. Methods

The viscoelastic material parameters are usually measured with a device referred to as a “rheometer”. A rotation-type strain-controlled rheometer is composed of a motor-driven part and the stress-detecting part. These parts are of cone-and plate shape (as was the case for the rheometer utilized in this thesis study) so that the local strain becomes uniform at all material points in the sample charged between the cone and plate parts. The other type of stress-controlled rheometer is equipped with a feed-back loop to control the stress generated by the strain. The cone-plate geometry ensuring the uniformity of the local strain is adopted also in this type of rheometer.

In the linear viscoelastic measurements, any type of strain/stress-evolution is accepted conceptually. Nevertheless, the dynamic oscillatory tests utilizing the sinusoidal strain or stress (eq 2-2) is usually adopted as the linear viscoelastic measurements, because the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, having different sensitivities to fast and slow relaxation modes are

simultaneously obtained from those measurements: Namely, the distribution of the relaxation intensity and time $\{h_p, \tau_p\}$ defined for the relaxation modulus is differently magnified in $G'(\omega)$ and $G''(\omega)$, as noted in the following expressions.²

$$G(t) = \sum_{p \geq 1} h_p \exp\left(-\frac{t}{\tau_p}\right) \quad (2-14)$$

$$G'(\omega) = \sum_{p \geq 1} h_p \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2}, \quad G''(\omega) = \sum_{p \geq 1} h_p \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad (2-15)$$

Equation (2-15), deduced from eqs (2-14) and (2-3), indicates that $G'(\omega)$ sensitively detects weak but slow modes (because the factor τ_p^2 in the numerator of the expression of G' significantly magnifies the contribution of such weak but slow mode to G'). In contrast, $G''(\omega)$ detects intensive but fast modes rather sensitively. This thesis study utilized these features of $G'(\omega)$ and $G''(\omega)$ to characterize the linear viscoelastic features of the HEUR aqueous solutions mostly with the dynamic oscillatory tests.

The nonlinear properties defined by eqs (2-10)-(2-13) are *not* mutually correlated through a platform equation like eq (2-1). For this reason, in this thesis study, the growth, decay, and steady state values of the shear stress and normal stress difference were separately measured and their deviations from the linear viscoelastic properties were discussed.

2-3. Fluorescence measurements

2-3-1. Principle³

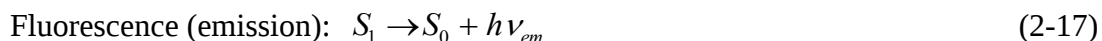
Fluorescence phenomenon occurs when an orbital electron of a molecule relaxes from its excited

state to ground state, as shown in the so-called Jablonski energy diagram illustrated in Figure 2-3.

Electrons of a molecule in the ground state, S_0 , adsorb a light at their excitation frequency ν_{ex} that has the energy $h\nu_{ex}$ (with h being the Planck's constant) thereby being activated to a higher energy state, S_1 :



S_1 consists of sub levels having different vibrational energies, and the excited electrons relax to the lowest vibrational level in S_1 via thermal dissipation of the energy due to coupling with the molecular vibration (that results in non-radiative relaxation), as shown in Figure 2-3. After this relaxation, the electrons transfer themselves to various vibrational levels in the ground state S_0 through emission of light at specific frequencies ν_{em} (having specific energies $h\nu_{em}$):



This emitted light is referred to as the fluorescent light.

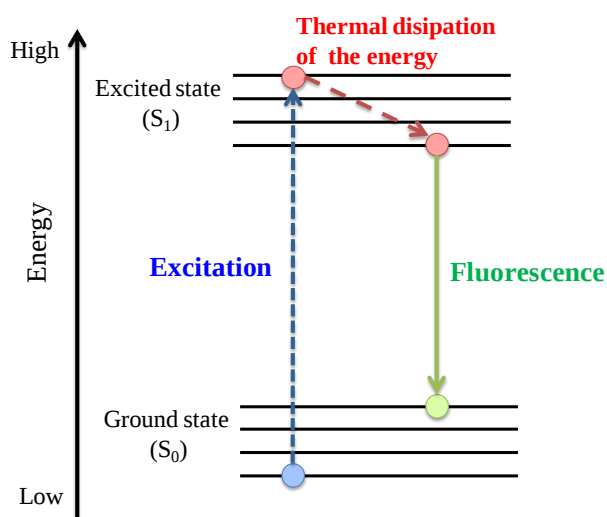
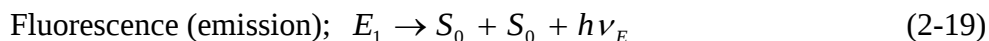


Figure 2-3. Schematic illustration of relaxation of the excited electrons.

When an unexcited molecule is spatially located within a neighborhood of an excited molecule,

these two molecules are associated with each other to form an excimer (excited state dimer), E_1 . The excimer exhibits fluorescent emission at frequencies ν_E to relax into two unactivated molecules in the ground state:



The electrons of the two molecules in the excimer interact with each other, so that the excimer fluorescent frequency ν_E is different from ν_{em} of excited/un-associated molecules (referred as monomer) and the fluorescent spectrum is wider for the excimer. Thus, the excimer and monomer can be readily distinguished optically.

This optical difference between the excimer and monomer in turn offers a convenient root for characterizing the association of fluorescent molecules. In solutions, those molecules could associate with each other to an extent determined by their concentration and the solvent quality. Specifically, the excimer is enriched when the solvent becomes poorer for the fluorescent molecules and/or those molecules are concentrated. This thesis study utilized pyrenyl groups at the HEUR chain ends as the optical probe to characterize their association state through analysis of the fluorescent spectrum.

2-3-2. Methods

Fluorescence spectrum is usually measured with a device referred to as a “fluorometer” consisting of a light source for excitation and a detector of fluorescent emission. Usually, the

fluorescence spectrum is measured for the excitation at a given (fixed) frequency, ν_{ex} .

In this thesis study, the fluorescence measurements were conducted for aqueous solution of HEUR having pyrenyl groups at the ends. The measurements were conducted in the quiescent state as well as under steady shear. Thus, the UV light (excitation light) source and the detector were installed to the stress-controlled rheometer having the cone-and-plate fixture made of quartz glass, as shown in Figure 2-4.

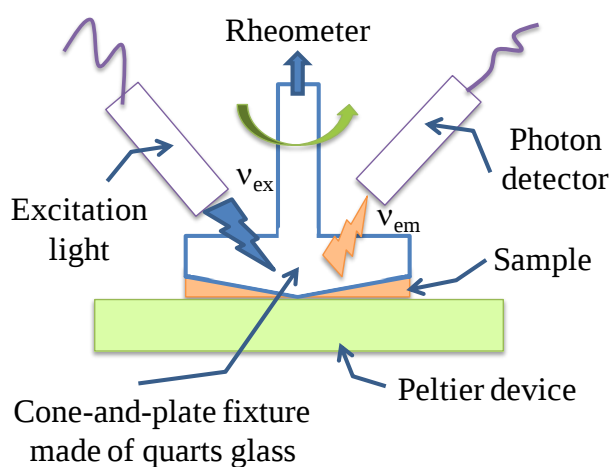


Figure 2-4. Schematic illustration of the device for measurement of fluorescence spectra under steady shear flow. Excitation light (UV light) source and detector were installed above the cone and plate fixture made of quartz glass.

References

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Chapter 3: Nonlinear Rheology of 1 wt% Hydrophobically Modified Ethoxylated Urethane (HEUR)

Aqueous Solution

3-1. Introduction

Hydrophobically-modified ethoxylated urethane (HEUR) is a representative telechelic polymer. As depicted in Figures 2-1 and 2-2, the main chain of HEUR is poly(ethylene oxide) (PEO), and short hydrophobic groups are attached to the chain ends through urethane groups. In aqueous solutions, those end groups associate through the hydrophobic interaction to form micellar cores, as explained in Chapter 2. At low concentration (still higher than the critical micellar concentration), the HEUR chains form so-called flower micelles. The core of this micelle is composed of hydrophobic end groups, and the corona is formed by hydrophilic PEO chains having the loop type conformation; cf. Figure 1-4. As the concentration is increased, the number density of flower micelles increases and the end groups of some chains are located in different cores to bridge the micelles. When the bridge fraction exceeds a percolation threshold, a huge network spreading throughout the whole solution is formed. The hydrophobic end groups are thermally detached from a core and eventually attached to the same and/or other core. Because of this thermal dissociation/association processes, the HEUR network is classified as a temporal network relaxing in a finite time scale.

Rheological properties of aqueous solutions of HEUR have been studied extensively¹⁻²¹, as explained in Chapter 1. The single-Maxwellian relaxation in the linear viscoelastic regime observed for relatively dilute HEUR aqueous solutions has been attributed to the thermal

reorganization (dissociation/association) of the HEUR network, and effects of temperature, concentration, and type of the end groups on the relaxation behavior have been also investigated^{3,8,11,22}.

Despite this simplicity in the linear regime, rheological properties of the HEUR solutions in the nonlinear regime are quite complicated. In particular, nontrivial behavior has been noted for the steady state shear viscosity. Concentrated HEUR solutions often exhibit shear thickening at intermediate shear rates and shear thinning at higher rates^{11,13,17}. The mechanism of this thickening/thinning behavior of HEUR solutions has been investigated with the aid of several models. One of the most frequently utilized models for telechelic polymers is the transient network type model. Focusing on the association/dissociation process of a target chain in the solution, Tanaka and Edwards²³⁻²⁶ formulated a transient network type model that naturally explains the single-Maxwellian relaxation in the linear regime. However, the original Tanaka-Edwards model does not explain the nonlinear shear thickening under fast flow. Thus, several mechanisms such as shear-enhanced formation of the network strands and the finite extensible nonlinear elasticity (FENE) of the strands were introduced into the model to mimic the thickening²³⁻³⁵. Despite this improvement, it is still controversial if the thickening results from the FENE effect or the shear-enhanced strand formation, or, the other mechanism(s), as explained in Chapter 1.

Thus, this chapter is devoted for further test of the thickening (and thinning) behavior of a rather dilute model HEUR solution (1 wt%) in a wide range of shear rates, $\dot{\gamma}$. Specifically, the focus is placed on the nonlinear rheological parameters explained in Chapter 2, the viscosity and first

normal stress coefficient growth functions after start-up of shear flow, $\eta^+(t;\dot{\gamma})$ and $\Psi_1^+(t;\dot{\gamma})$, their steady state values, $\eta(\dot{\gamma}) = \eta^+(\infty;\dot{\gamma})$ and $\Psi_1(\dot{\gamma}) = \Psi_1^+(\infty;\dot{\gamma})$, and the viscosity and first normal stress coefficient decay functions after cessation of steady flow, $\eta^-(t;\dot{\gamma})$ and $\Psi_1^-(t;\dot{\gamma})$. The test clearly indicated that the thickening seen for $\eta^+(t;\dot{\gamma})$ and $\eta(\dot{\gamma})$ at intermediate $\dot{\gamma}$ was associated with no nonlinearity of $\Psi_1^+(t;\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ and that the relaxation times of $\eta^-(t;\dot{\gamma})$ and $\Psi_1^-(t;\dot{\gamma})$ coincide with those in the linear regime. These results suggest that the factors so far considered, the FENE effect and the shear-induced increase of the strand number density, are not important for the thickening of $\eta^+(t;\dot{\gamma})$ and $\eta(\dot{\gamma})$ observed the 1 wt% HEUR solution. Instead, the thickening can be related to re-association of the HEUR strands that occurs in balance with the dissociation but anisotropically enhanced in the shear gradient direction, as suggested from a simple analysis based on a transient network type model. These results are summarized below together with the thinning feature of the solution attributable to flow-induced disruption of the network.

3-2. Experimental

HEUR having hexadecane groups at the chain ends (cf. Table 2-1) was utilized. The material subjected to the rheological measurements was a 1.0 wt% aqueous solution of this HEUR sample in distilled water. Prescribed masses of water and HEUR were stirred for 24 hours to prepare the solution.

For this 1.0 wt% aqueous HEUR solution, rheological measurements were conducted with laboratory rheometers, MCR-301 (Anton Paar) and ARES-G2 (TA Instruments). MCR-301 is a

stress-controlled rheometer, whereas ARES-G2 is a strain-controlled rheometer.

Dynamic measurements in the linear viscoelastic regime were made with MCR-301 in a cone-plate (CP) geometry (diameter $d = 75$ mm, cone angle $\theta = 1.0^\circ$) at several temperatures T between 5 and 25°C. The measurement at 25°C was made also with ARES-G2 in a CP geometry ($d = 25$ mm, $\theta = 2.3^\circ$). The storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ measured as functions of the angular frequency ω , obeyed the time-temperature superposition at low ω where the HEUR network exhibited the terminal relaxation (through its thermal reorganization). Those data were reduced at 25°C.

The viscosity and first normal stress coefficient growth functions after start-up of shear flow, $\eta^+(t; \dot{\gamma})$ and $\Psi_1^+(t; \dot{\gamma})$, the steady state viscosity and the steady state first normal stress coefficient, $\eta(\dot{\gamma}) = \eta^+(\infty; \dot{\gamma})$ and $\Psi_1(\dot{\gamma}) = \Psi_1^+(\infty; \dot{\gamma})$, and the viscosity and first normal stress coefficient decay functions after cessation of steady shear, $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, were measured at 25°C with ARES-G2 in the CP geometry ($d = 25$ mm, $\theta = 2.3^\circ$) at several shear rates $\dot{\gamma}$ between 0.05 and 100 s⁻¹. $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ were measured also with MCR-301 in the CP geometry ($d = 75$ mm, $\theta = 1.0^\circ$).

3-3. Results

3-3-1. Linear viscoelastic behavior.

For the 1.0 wt% aqueous HEUR solution, Figure 3-1 shows the master curves of storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, reduced at 25°C. (The data measured with the stress- and

strain-controlled rheometers, MCR-301 and ARES-G2, agreed with each other.) The thick curves indicate the result of fitting with the single-Maxwellian model:

$$G'(\omega) = G_0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}, \quad G''(\omega) = G_0 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (3-1)$$

Here, G_0 (= 15 Pa) and τ (= 0.45 s) are the characteristic modulus and relaxation time, respectively.

These G_0 and τ values are close to those reported for a similar HEUR solution. The Maxwellian fit is excellently achieved except at high ω where the time-temperature superposition fails, as noted also in the previous studies.^{7,12} This failure is later discussed in Chapter 4 in relation to the local motion of the HEUR chains.

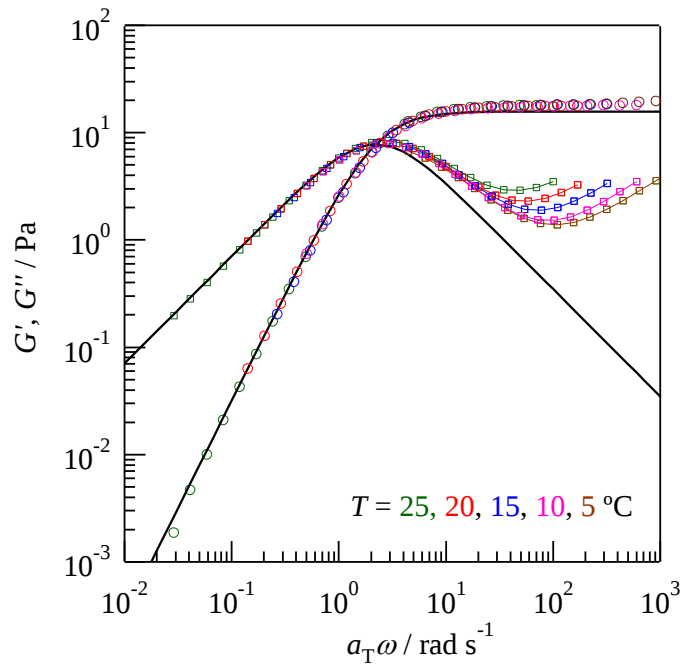


Figure 3-1. Storage and loss moduli, G' and G'' , measured for the 1.0 wt% aqueous solution of HEUR reduced at 25°C. Symbols represent the experimental data (after time-temperature superposition), and the thick curves show the results of fitting with the single-Maxwell model.

The single-Maxwellian behavior of the HEUR solution has been attributed to the thermal reorganization (dissociation/association) of the transient network occurring at the time τ , and G_0 has been related to the entropy elasticity of the HEUR strands in the network. From the G_0 value, the

number density ν of active strands can be estimated as

$$\nu = \frac{G_0}{k_B T} \cong 3.7 \times 10^{21} \text{ m}^{-3} \quad (3-2)$$

where k_B is the Boltzmann constant and T is the absolute temperature. This ν value is much smaller than the number density of the HEUR chains, $\nu_0 = 1.8 \times 10^{23} \text{ m}^{-3}$ evaluated from the HEUR concentration (0.01 g cm^{-3}) and molecular weight ($M_n = 3.4 \times 10^4$): $\nu/\nu_0 = 0.021$, which is close to the ν/ν_0 ratio reported previously^{3,6}. Thus, the connected sequence of bridges (superbridge) of the flower micelles should behave as the active strand, although some fraction of those strings would be of loop-type and not involved in the active strands.

Additional information for the HEUR network can be found in Figure 3-2 where the natural logarithm of the shift factor for the G' and G'' master curve, $\ln a_T$, is plotted against T^{-1} . The well-known Arrhenius behavior, $\ln a_T = E_a(T^{-1} - T_r^{-1})/R$ with R being the gas constant, is clearly observed, and the activation energy is evaluated to be $E_a = 88 \text{ kJ mol}^{-1}$. This E_a value, close to the data reported for similar HEUR solutions^{17,22}, can be assigned as the association energy of the hexadecyl groups at the HEUR chain ends that stabilizes the HEUR network.

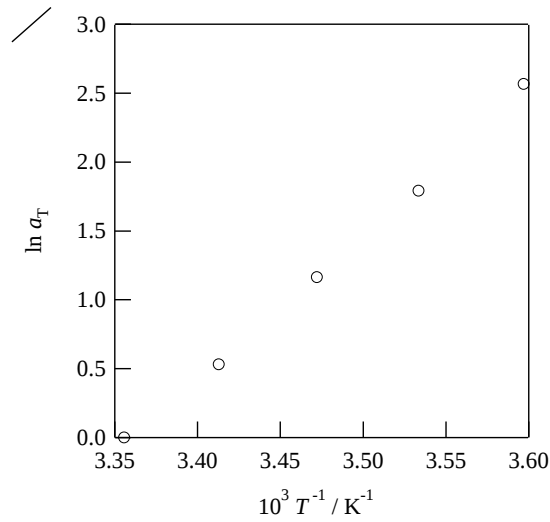


Figure 3-2. Time-temperature shift factor a_T for the 1.0 wt% aqueous solution of HEUR in the linear viscoelastic regime. The circles show the data, and the solid line represents the Arrhenius equation.

3-3-2. Nonlinear flow behavior.

For the 1.0 wt% HEUR solution at 25°C, Figures 3-3 and 3-4 show the viscosity and first normal stress coefficient growth functions after start-up of shear flow, $\eta^+(t; \dot{\gamma})$ and $\Psi_1^+(t; \dot{\gamma})$. These data were obtained with the strain-controlled rheometer, ARES-G2. The numbers indicate the shear rate $\dot{\gamma}$ (s^{-1}). For clarity of the plots, only representative data are shown.

Figure 3-5 shows the corresponding steady state viscosity and first normal stress coefficient, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$. The data shown with unfilled and filled symbols were obtained with the stress- and strain-controlled rheometers, MCR-301 and ARES-G2, respectively. The data obtained with these rheometers agree with each other.

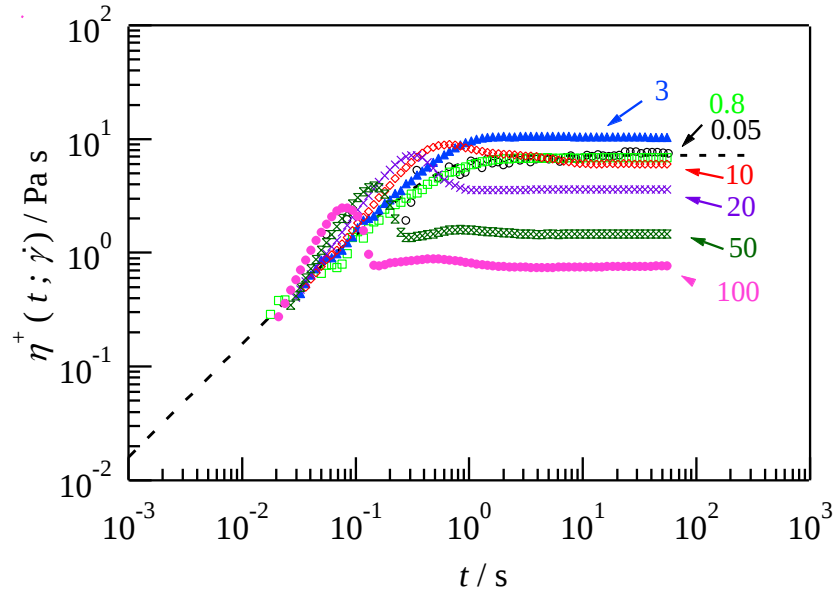


Figure 3-3. Shear viscosity growth function $\eta^+(t; \dot{\gamma})$ of the 1.0 wt% HEUR aqueous solution at 25°C measured at various shear rates, $\dot{\gamma}/s^{-1} = 0.05, 0.8, 3, 10, 20, 50$, and 100. The dashed curve represents the growth function $\eta^+(t; \dot{\gamma})$ in the linear viscoelastic regime ($\dot{\gamma} \rightarrow 0$) evaluated from the G' and G'' data.

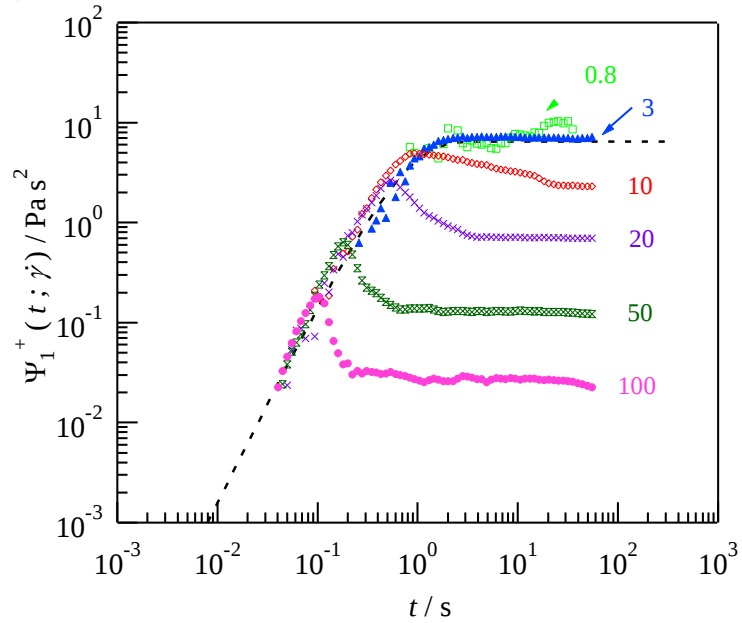


Figure 3-4. First normal stress coefficient growth function $\Psi_1^+(t; \dot{\gamma})$ of the 1.0 wt% HEUR aqueous solution at 25°C measured at various shear rates, $\dot{\gamma}/s^{-1} = 0.8, 3, 10, 20, 50$, and 100. The dashed curve represents the growth function $\Psi_1^+(t; \dot{\gamma})$ in the linear viscoelastic regime ($\dot{\gamma} \rightarrow 0$) evaluated from the G' and G'' data.

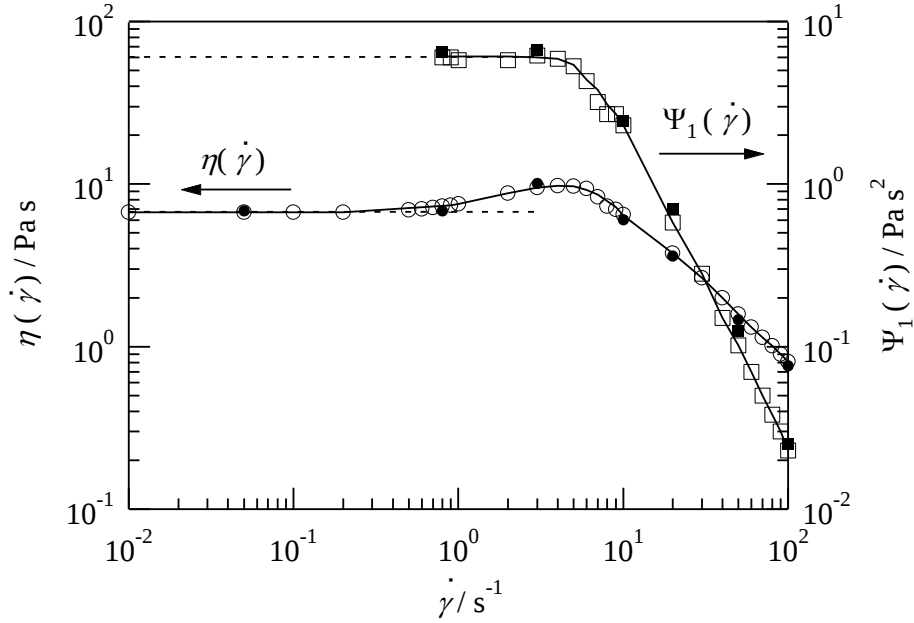


Figure 3-5. Steady state shear viscosity $\eta(\dot{\gamma})$ and steady state first normal stress coefficient $\Psi_1(\dot{\gamma})$ measured for the 1.0 wt% aqueous solution of HEUR at 25°C. The unfilled and filled symbols indicate the data obtained with the stress- and strain-controlled rheometers, MCR-301 and ARES-G2, respectively. Horizontal dashed lines indicate η_0 and $\Psi_{1,0}$ in the linear viscoelastic regime ($\dot{\gamma} \rightarrow 0$) evaluated from the G' and G'' data.

Since the HEUR solution exhibits the single-Maxwellian behavior of G' and G'' (cf. Figure 3-1), the growth functions in the linear viscoelastic regime, $\eta^+(t)$ and $\Psi_1^+(t)$, and the zero-shear viscosity and normal stress coefficient, η_0 and $\Psi_{1,0}$, can be analytically calculated as (cf. eqs (2-6)-(2-8)):

$$\eta^+(t) = G_0 \tau [1 - \exp(-t/\tau)], \quad \eta_0 = G_0 \tau \quad (3-3)$$

$$\Psi_1^+(t) = 2G_0 \tau^2 [1 - \exp(-t/\tau) - (t/\tau) \exp(-t/\tau)], \quad \Psi_{1,0} = 2G_0 \tau^2 \quad (3-4)$$

where G_0 ($= 15$ Pa) and τ ($= 0.45$ s) are the characteristic modulus and relaxation time determined for the G' and G'' data. These $\eta^+(t)$ and $\Psi_1^+(t)$ are shown with the dashed curves in Figures 3-3 and 3-4, and η_0 and $\Psi_{1,0}$, with the horizontal dashed lines in Figure 3-5.

At shear rates well below the equilibrium relaxation frequency $1/\tau$ ($= 2.2$ s $^{-1}$), the linear

viscoelastic flow behavior is observed in Figures 3-3 and 3-4. Namely, the $\eta^+(t; \dot{\gamma})$ data for $\dot{\gamma} = 0.05$ and 0.8 s^{-1} agree with the linear $\eta^+(t)$ within experimental uncertainty, and the $\Psi_1^+(t; \dot{\gamma})$ data for $\dot{\gamma} = 0.8 \text{ s}^{-1}$ agree with the linear $\Psi_1^+(t)$. (At $\dot{\gamma} = 0.05 \text{ s}^{-1}$, the measured normal stress difference was too small to give the $\Psi_1^+(t; \dot{\gamma})$ data accurately and thus those data are not shown in Figure 5. However, $\Psi_1^+(t; \dot{\gamma})$ at such low $\dot{\gamma}$ should agree with $\Psi_1^+(t)$.) Correspondingly, the $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ data at $\dot{\gamma} \ll 1/\tau$ agree with the linear η_0 and $\Psi_{1,0}$, as noted in Figure 3-5.

On an increase of $\dot{\gamma}$ from 1 s^{-1} ($= 0.45/\tau$) to 5 s^{-1} ($= 2.2/\tau$), the viscosity exhibits a moderate increase (moderate thickening). For example, for $\dot{\gamma} = 3.0 \text{ s}^{-1}$, the $\eta^+(t; \dot{\gamma})$ data monotonically grow, without exhibiting overshoot, to a level above $\eta^+(t)$ (cf. Figure 3-3), and $\eta(\dot{\gamma})$ is larger than η_0 by a factor of E 45 % (cf. Figure 3-5). However, the $\Psi_1^+(t; \dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ data at $\dot{\gamma} < 5 \text{ s}^{-1}$ remain close to the linear $\Psi_1^+(t)$ and $\Psi_{1,0}$, as noted in Figures 3-4 and 3-5. Namely, the thickening of $\eta^+(t; \dot{\gamma})$ and $\eta(\dot{\gamma})$ is associated with *no* nonlinearity of $\Psi_1^+(t; \dot{\gamma})$ and $\Psi_1(\dot{\gamma})$.

Both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ begin to decrease on a further increase of $\dot{\gamma}$ above 5 s^{-1} , as seen in Figure 3-5. This thinning behavior is characterized by power-law relations at high $\dot{\gamma}$,

$$\eta(\dot{\gamma}) \propto \dot{\gamma}^{-0.97}, \quad \Psi_1(\dot{\gamma}) \propto \dot{\gamma}^{-1.98} \quad (\text{for } \dot{\gamma} > 30 \text{ s}^{-1}) \quad (3-5)$$

Thus, the thinning at high $\dot{\gamma}$ is characterized with $\dot{\gamma}$ -insensitive shear stress ($\sigma \propto \dot{\gamma}^{0.03}$) and first normal stress difference ($N_1 \propto \dot{\gamma}^{0.02}$). It should be also noted that the thinning behavior is qualitatively different for $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$. The thinning of $\eta(\dot{\gamma})$ is associated with a transient overshoot of $\eta^+(t; \dot{\gamma})$ well above the linear $\eta^+(t)$ (cf. Figure 3-3), whereas the thinning of $\Psi_1(\dot{\gamma})$ is associated with no significant overshoot of $\Psi_1^+(t; \dot{\gamma})$ (very weak overshoot, if any)

above the linear $\Psi_1^+(t)$ (cf. Figure 3-4).

As explained above, the 1.0 wt% HEUR solution exhibits characteristic thickening and thinning behavior commonly observed for solutions of telechelic polymers. The thickening and thinning obviously indicate that the HEUR network exhibits some structural change under shear. This change can be monitored through the stress decay after cessation of the steady shear. Thus, the viscosity and normal stress coefficient decay functions, $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, were measured with the strain-controlled rheometer, ARES-G2. As representative examples, the data measured for $\dot{\gamma} = 3$ and 20 s^{-1} (in the thickening and thinning regimes for $\eta(\dot{\gamma})$) are shown in Figures 3-6 and 3-7, respectively. The $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ data at short t unequivocally reflect the HEUR network structure under steady shear (just before cessation of shear). The initial values, $\eta^-(0; \dot{\gamma})$ and $\Psi_1^-(0; \dot{\gamma})$, agreed with the steady state values, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$, which lends support to this argument for the data at short t .

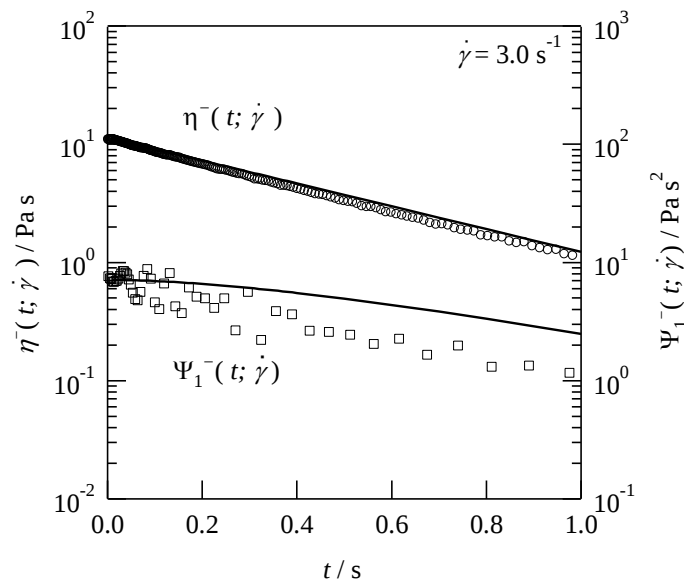


Figure 3-6. Shear viscosity and first normal stress coefficient decay functions, $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, measured for the 1.0 wt% HEUR aqueous solution pre-sheared at $\dot{\gamma} = 3.0 \text{ s}^{-1}$ (in the thickening regime for $\eta(\dot{\gamma})$) at 25°C . The solid curves indicate the linear $\eta^-(t)$ and $\Psi_1^-(t)$ with adjustment made only for their initial values.

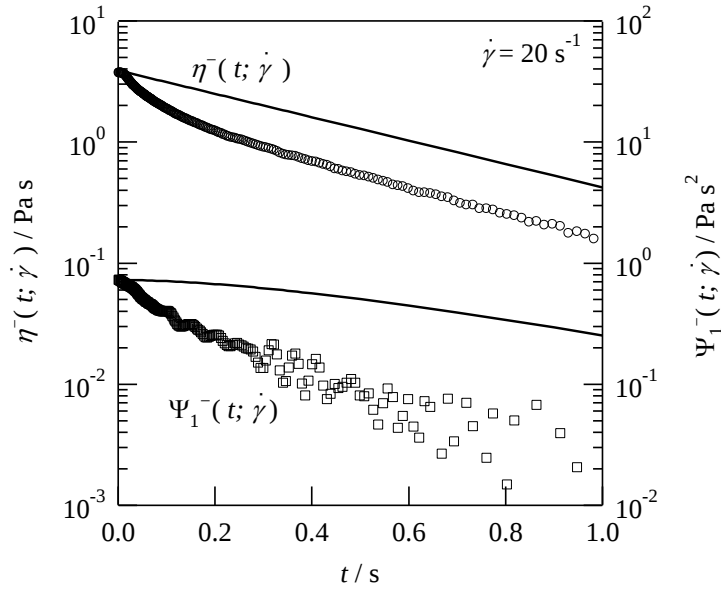


Figure 3-7. Shear viscosity and first normal stress coefficient decay functions, $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, measured for the 1.0 wt% HEUR aqueous solution pre-sheared at $\dot{\gamma} = 20 \text{ s}^{-1}$ (in the thinning regime for both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$) at 25°C. The solid curves indicate the linear $\eta^-(t)$ and $\Psi_1^-(t)$ with adjustment made only for their initial values.

In the linear regime, the decay functions are analytically expressed in terms of the time τ and modulus G_0 associated to the single-Maxwellian relaxation (cf. eqs (2-5) and (2-7)):

$$\eta^-(t) = \eta_0 \exp(-t/\tau) \quad \text{with} \quad \eta_0 = G_0 \tau \quad (3-6)$$

$$\Psi_1^-(t) = \Psi_{1,0} \left\{ 1 + \frac{t}{\tau} \right\} \exp(-t/\tau) \quad \text{with} \quad \Psi_{1,0} = 2G_0 \tau^2 \quad (3-7)$$

The solid curves in Figures 3-6 and 3-7 indicate these linear decay functions with the initial values being adjusted for the nonlinearity, $\{\eta_1(\dot{\gamma})/\eta_0\} \eta^-(t)$ and $\{\Psi_1(\dot{\gamma})/\Psi_{1,0}\} \Psi_1^-(t)$. In the thickening regime (Figure 3-6), these curves are close to the $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ data in particular at short t where the data reflect the HEUR network structure just before cessation of shear. A rapid initial decay of $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, that characterizes the finite extensible nonlinear elasticity (FENE)-type nonlinear effect in the thickening regime *if any*, is not detected experimentally. This

result strongly suggests that the dissociation time of the HEUR network under shear agrees with τ in the linear regime and that the network structure under shear is not too much different from that at equilibrium. (The scatter of the $\Psi_1^-(t; \dot{\gamma})$ data points at short t is mainly due to a mechanical noise in the shear-gradient direction on cessation of steady shear.)

In contrast, in the thinning regime (Figure 3-7), the initial decay of the $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ data is considerably faster than that in the linear regime (solid curves). This result suggests that the HEUR network is largely disrupted and the fragmented network strands are considerably stretched by the shear in the thinning regime to exhibit fast contraction process of the strands at $t \ll \tau$. The decay of $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ at longer t becomes as slow as that in the linear regime, possibly due to the thermal reorganization of the remaining network (that could also grow through association of the fragmented strands during the stress decay process).

The above decay behavior is quite informative for discussion of the thickening and thinning behavior of the HEUR solution, as explained later. For this discussion, it is also informative to compare the behavior of wormlike micelles of surfactants formed in water with the behavior of the HEUR solution. Extensive studies^{5, 37-40} revealed that the wormlike micelles of cetyl trimethyl ammonium bromide (CTAB) and sodium salicylate (NaSal) (1:1 molar ratio) exhibit the single-Maxwellian linear viscoelasticity very similar to that of the HEUR solution. Concentrated CTAB/NaSal (1/1) solutions under fast shear exhibit increases of both $\eta^+(t; \dot{\gamma})$ and $\Psi_1^+(t; \dot{\gamma})$ to levels well above the linear $\eta^+(t)$ and $\Psi_1^+(t)$, and this thickening behavior is attributed to the FENE, i.e., stretch-hardening of the wormlike micelles themselves, as reported by Inoue et al³⁸.

The thickening behavior of the HEUR solution is quite different: The thickening of $\eta^+(t; \dot{\gamma})$ and $\eta(\dot{\gamma})$ of the HEUR solution is associated with the linear behavior of $\Psi_1^+(t; \dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ and thus not attributable to the simple FENE effect of the HEUR strands.

Comparison of the thinning behavior of entangled polymers with that of the HEUR solution (at high $\dot{\gamma} > 5 \text{ s}^{-1}$) is also useful for elucidating the thinning mechanism in the HEUR solution. The thinning of entangled polymers due to strong shear-orientation of the chains can be characterized by the power-law relationships^{41,42}:

$$\eta(\dot{\gamma}) \propto \dot{\gamma}^{-0.82} \text{ and } \Psi_1(\dot{\gamma}) \propto \dot{\gamma}^{-1.5 \pm 0.05} \text{ for monodisperse linear chains} \quad (3-8)$$

The $\dot{\gamma}$ dependence of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ of the HEUR solution in the thinning regime (eq 3-5) is considerably stronger than that for entangled polymers specified by eq 3-8. Thus, the thinning of the HEUR solution is not attributable to the simple shear orientation without the network reorganization.

3-4. Discussion

3-4-1. Test of conventional thickening mechanisms for HEUR solution

In the studies so far conducted for HEUR solutions, the shear thickening has been attributed to either the finite extensible nonlinear elasticity (FENE) of the shear-stretched HEUR strands or the increase of the effective strand number density on shear-induced reorganization of the network (shear-enhanced strand formation). In principle, both mechanisms could lead to the thickening, and the origin of the thickening has remained controversial. However, the results shown in the

previous subsections shed light on this problem.

The FENE concept is widely utilized for constitutive equations of polymers⁴³. Koga and Tanaka²³⁻²⁶ improved the expression of the network dissociation rate in the transient FENE network model but assumed the network reformation to occur randomly/isotropically in space. Indei^{34,35} showed that the transient FENE network model does not always predict the thickening because of competition between the stress-enhancing FENE effect and the stress-suppressing dissociation effect. Nevertheless, in a considerably wide range of the shear rate $\dot{\gamma}$ where the former overwhelms the latter, Koga-Tanaka model predicts the thickening of *both* viscosity and first normal stress coefficient³¹. Several experimental results were reported to be in favor of this FENE-induced thickening deduced from the Koga-Tanaka model. For example, Berret et al.^{9,10} conducted start-up flow experiments for HEUR solutions and attributed the thickening of the viscosity to the increase of the effective modulus due to the FENE effect. Pellens et al.^{13,14,20} reported that the stress-optical rule (SOR), being valid only in the absence of the FENE effect, fails for their HEUR solutions in the thickening regime and thus the thickening is related to the FENE effect, although the reported increase of the $\eta(\dot{\gamma})/\eta_0$ ratio is only by 1-2 %. (A much stronger FENE effect has been confirmed for both viscosity and first normal stress coefficient of the wormlike micelles³⁸.)

However, the 1.0 wt% HEUR solution examined in this chapter exhibits the thickening of the viscosity ($\eta^+(t;\dot{\gamma})$ and $\eta(\dot{\gamma})$) while allowing the first normal stress coefficient ($\Psi_1^+(t;\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$) to stay in the linear regime (cf. Figures 3-3, 3-4, and 3-5). In addition, the network strands

being highly stretched under shear (to a FENE level) should exhibit fast contraction on cessation of shear, but no such fast process is not observed for the $\eta^-(t;\dot{\gamma})$ and $\Psi_1^-(t;\dot{\gamma})$ data of the HEUR solution in the thickening regime (Figure 3-6). Thus, the thickening of the 1.0 wt% HEUR solution is concluded to be not primarily due to the simple FENE effect. In fact, this conclusion is in harmony with a simple but unambiguous analysis comparing the elastic energy of the HEUR strand and the association energy of the end groups of the HEUR chains, as explained in Appendix 3A.

Concerning the above conclusion, it should be noted that the Koga-Tanaka model incorporates the FENE effect as one of the essential ingredients but does not always predicts thickening of both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ ³¹: The model includes two basic parameters A and g , with A representing the FENE contribution to the strand tension and g representing an effect of chain tension on the dissociation rate of the HEUR network. The nonlinear rheological behavior of the model including the shear thinning and thickening are mainly determined by competition of the nonlinear elasticity (controlled by A) and the acceleration of the dissociation (controlled by g). The thickening of $\eta(\dot{\gamma})$ and thinning of $\Psi_1(\dot{\gamma})$ could be simultaneously deduced from the Koga-Tanaka model for a specific combination of the parameters. For example, slight thickening of $\eta(\dot{\gamma})$ associated with slight thinning of $\Psi_1(\dot{\gamma})$ (both $\sim 10\%$ in magnitude) reported in Ref.31 are fairly well described by the model, although some deviation is noted for the prediction of $\Psi_1(\dot{\gamma})$; see Figure 10 of Ref.31. However, the parameters giving this description were $A = 5$ and $g = 0.16$, with the former giving a significant FENE effect in a case of the strand stretching.

The FENE effect is not important for the 1.0 wt% HEUR solution examined here, as explained above. Thus, if the Koga-Tanaka model is to apply to that HEUR solution, the parameter A is to be set in a close vicinity of zero. Then, the other parameter g should be also set to be close to zero so as to reproduce the lack of thinning/thickening of $\Psi_1(\dot{\gamma})$ in the thickening zone of $\eta(\dot{\gamma})$, as clearly noted from Figure 4 of Ref.31. For that case, the Koga-Tanaka model reduces to the Green-Tobolsky type transient network model⁴⁴ considering no effect of chain tension on the strand dissociation rate.

Thus, for the HEUR solution examined in this thesis study, a general discussion should be made within the context of the Gaussian transient network model that allows anisotropic formation of the HEUR network strands under shear. This discussion is given in the next subsection.

Conventionally, the increase of the effective strand number density ν under shear has been also considered as a possible mechanism of shear thickening. Indeed, some experimental data for HEUR solutions were reported to be not in accord to the FENE network model but support the model considering this increase of ν ^{12,15,16}. For example, Tam et al.¹⁵ conducted shear experiments with parallel superposition of small amplitude oscillation to find decrease and increase, respectively, of the relaxation time and the characteristic modulus defined for the superposed oscillation. This result led them to attribute the thickening to the increase of ν . François et al.¹⁶ performed small angle neutron scattering under shear and reported that the internal structure of the micellar core is not affected by flow in the thickening region. This shear insensitivity of the core structure is in harmony with the model considering the increase of ν . Nevertheless, this model

results in simultaneous increases (simultaneous thickening) of the viscosity and normal stress coefficient, which does not match the behavior of the 1.0 wt% HEUR solution examined in this chapter.

Thus, neither the transient FENE network model nor the model considering the flow-induced increase of ν can explain the thickening of $\eta(\dot{\gamma})$ and lack of nonlinearity of $\Psi_1(\dot{\gamma})$ seen in Figures 3-4, 3-5, and 3-6 for our HEUR solution. On the basis of this experimental fact, a simple, transient Gaussian network model (without FENE/increase of ν) is formulated in the following subsection to discuss the thickening behavior of the 1.0 wt% HEUR solution.

3-4-2. Simple transient Gaussian network model for steady state shear thickening

The thickening behavior of the 1.0 wt% HEUR solution is governed by neither the FENE effect nor the shear-induced increase of number density ν of the active strands, as discussed above. Thus, the HEUR strands should be in the essentially Gaussian state (not stretch-hardened) and have the constant ν even under the shear in the thickening regime. Then, the steady state viscosity and normal stress coefficient are expressed in terms of the end-to-end vector $\mathbf{r}$ of the network strands as (cf. eq (1-6))^{43,45}

$$\eta(\dot{\gamma}) = \frac{3k_B T}{r_0^2} \frac{\nu}{\dot{\gamma}} \int d\mathbf{r} r_x r_y \psi_{ss}(\mathbf{r}, \dot{\gamma}) \quad (3-9)$$

$$\Psi_1(\dot{\gamma}) = \frac{3k_B T}{r_0^2} \frac{\nu}{\dot{\gamma}^2} \int d\mathbf{r} (r_x^2 - r_y^2) \psi_{ss}(\mathbf{r}, \dot{\gamma}) \quad (3-10)$$

Here, k_B and T are the Boltzmann constant and absolute temperature, respectively, and r_x and r_y indicate the components of $\mathbf{r}$ in the shear and shear gradient directions. $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ is the steady

state distribution function of $\mathbf{r}$ under the shear at $\dot{\gamma}$. In eqs 3-9 and 3-10, all network strands are approximated to have the same average size r_0 at equilibrium and have the Gaussian spring constant, $3k_B T/r_0^2$, irrespective of their stretch ratio.

In eqs 3-9 and 3-10, all nonlinearities emerge from the deviation of $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ from the equilibrium distribution function,

$$\psi_{eq}(\mathbf{r}) = \left(\frac{3}{2\pi r_0^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{r}^2}{2r_0^2} \right) \quad (3-11)$$

This deviation is not trivial because the reorganization kinetics of the network should be affected by the shear flow. For description of this deviation in the thickening regime, it is necessary to adopt a simplified but analytically tractable version of the transient network model considering dissociation/association of the active, Gaussian strands having the constant number density ν in total. None of the thickening mechanisms explained in the previous subsection is incorporated in the model.

In the model formulated here, the dynamics of the system is simply described by the probability distribution function of the active strands. Specifically, $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ in the model is deduced from a birth-and-death type master equation for those strands after start-up of shear at $\dot{\gamma}$:

$$\frac{\partial \psi(\mathbf{r}, t, \dot{\gamma})}{\partial t} = -\dot{\gamma}_y \frac{\partial \psi(\mathbf{r}, t, \dot{\gamma})}{\partial r_y} - \frac{1}{\tau_0} \psi(\mathbf{r}, t, \dot{\gamma}) + \frac{1}{\tau_0} \phi(\mathbf{r}, t, \dot{\gamma}) \quad (3-12)$$

Here, $\psi(\mathbf{r}, t, \dot{\gamma})$ is the probability distribution function of $\mathbf{r}$ of the strand at time t , τ_0 is the characteristic time for the dissociation and association, and $\phi(\mathbf{r}, t, \dot{\gamma})$ is the source function, i.e., probability distribution function of $\mathbf{r}$ of the newly created (associated) network strands at t . At

equilibrium, both $\psi(\mathbf{r}, t, \dot{\gamma} = 0)$ and $\phi(\mathbf{r}, t, \dot{\gamma} = 0)$ coincide with the equilibrium distribution function $\psi_{eq}(\mathbf{r})$ given by eq 3-11. Furthermore, τ_0 is equal to τ for the single-Maxwellian relaxation in the linear viscoelastic regime.

In contrast, under steady shear, $\partial\psi/\partial t = 0$ so that eq 3-12 specifies a relation between $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ and $\phi_{ss}(\mathbf{r}, \dot{\gamma})$, with the subscript “ss” standing for the t -independent functions in the steady flow state:

$$\dot{\gamma} \frac{\partial \psi(\mathbf{r}, t, \dot{\gamma})}{\partial r_y} + \frac{1}{\tau_0} \psi(\mathbf{r}, t, \dot{\gamma}) = \frac{1}{\tau_0} \phi(\mathbf{r}, t, \dot{\gamma}) \quad (3-13)$$

Thus, some general features of the nonlinear properties under steady shear can be found from the anisotropy of $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ (cf. eq 3-9 and 3-10) and thus of $\phi_{ss}(\mathbf{r}, \dot{\gamma})$, without too much details of the re-association mechanism.

For relatively small $\dot{\gamma}$ (where the thickening is actually observed for the HEUR solution), $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ and $\phi_{ss}(\mathbf{r}, \dot{\gamma})$ can be expanded around their Gaussian forms at equilibrium, $\psi_{ss}(\mathbf{r}, 0) = \phi_{ss}(\mathbf{r}, 0) = \psi_{eq}(\mathbf{r})$. This expansion can be conveniently made with the aid of the Hermite polynomials being utilized as the expansion basis:

$$\psi_{ss}(\mathbf{r}, \dot{\gamma}) = \psi_{eq}(\mathbf{r}) \sum_{n,m,l=0}^{\infty} a_{n,m,l}(\dot{\gamma}) 2^{-(n+m+l)/2} H_n\left(\frac{\sqrt{3}r_x}{\sqrt{2}r_0}\right) H_m\left(\frac{\sqrt{3}r_y}{\sqrt{2}r_0}\right) H_l\left(\frac{\sqrt{3}r_z}{\sqrt{2}r_0}\right) \quad (3-14)$$

$$\phi_{ss}(\mathbf{r}, \dot{\gamma}) = \psi_{eq}(\mathbf{r}) \sum_{n,m,l=0}^{\infty} b_{n,m,l}(\dot{\gamma}) 2^{-(n+m+l)/2} H_n\left(\frac{\sqrt{3}r_x}{\sqrt{2}r_0}\right) H_m\left(\frac{\sqrt{3}r_y}{\sqrt{2}r_0}\right) H_l\left(\frac{\sqrt{3}r_z}{\sqrt{2}r_0}\right) \quad (3-15)$$

Here, $a_{n,m,l}$ and $b_{n,m,l}$ are the expansion coefficients and $H_n(x)$ is the n -th order Hermite polynomial⁴⁶. From eqs 3-13, 3-14, and 3-15 with the aid of the recurrence formula, $H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x)$ and $dH_n(x)/dx = 2nH_{n-1}(x)$, the coefficients $a_{n,m,l}$ and $b_{n,m,l}$ are mutually

related with each other. For low-order coefficients necessary for calculation of $\eta(\dot{\gamma})$ and $\Psi_1^+(\dot{\gamma})$ up to the order of $\dot{\gamma}^2$ (up to the lowest order of nonlinearity), the relations are summarized as

$$a_{1,1,0}(\dot{\gamma}) = b_{1,1,0}(\dot{\gamma}) + (\tau_0 \dot{\gamma})[1 + 2b_{0,2,0}(\dot{\gamma})] \quad (3-16a)$$

$$a_{0,2,0}(\dot{\gamma}) = b_{0,2,0}(\dot{\gamma}) \quad (3-17b)$$

$$a_{2,0,0}(\dot{\gamma}) = b_{2,0,0}(\dot{\gamma}) + (\tau_0 \dot{\gamma})b_{1,1,0}(\dot{\gamma}) + (\tau_0 \dot{\gamma})^2[1 + 2b_{0,2,0}(\dot{\gamma})] \quad (3-18c)$$

The $\dot{\gamma}$ dependence of these low-order coefficients can be found from simple consideration.

First of all, the normalization condition for $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ and $\phi_{ss}(\mathbf{r}, \dot{\gamma})$ gives $\dot{\gamma}$ -independent coefficients, $a_{0,0,0}(\dot{\gamma}) = b_{0,0,0}(\dot{\gamma}) = 1$. Furthermore, from the symmetry of $\psi_{ss}(\mathbf{r}, \dot{\gamma})$ and $\phi_{ss}(\mathbf{r}, \dot{\gamma})$ under simple shear field, $a_{n,m,l}(\dot{\gamma})$ and $b_{n,m,l}(\dot{\gamma})$ can have non-zero values only when both $(n + m)$ and l are even integers. Finally, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ are required to be even functions of $\dot{\gamma}$ (to be invariant on reversal of the shear direction) and converge to η_0 and $\Psi_{1,0}$ (cf. eqs 3-3 and 3-4) for $\dot{\gamma} \rightarrow 0$. This requirement forces the low-order coefficients shown above to have the following form of expansion with respect to $\dot{\gamma}$:

$$b_{1,1,0}(\dot{\gamma}) = b_{1,1,0}^{(3)} \{\tau_0 \dot{\gamma}\}^3 + O(\{\tau_0 \dot{\gamma}\}^5) \quad (3-17a)$$

$$b_{2,0,0}(\dot{\gamma}) = b_{2,0,0}^{(2)} \{\tau_0 \dot{\gamma}\}^2 + b_{2,0,0}^{(4)} \{\tau_0 \dot{\gamma}\}^4 + O(\{\tau_0 \dot{\gamma}\}^6) \quad (3-17b)$$

$$b_{0,2,0}(\dot{\gamma}) = b_{0,2,0}^{(2)} \{\tau_0 \dot{\gamma}\}^2 + b_{0,2,0}^{(4)} \{\tau_0 \dot{\gamma}\}^4 + O(\{\tau_0 \dot{\gamma}\}^6) \quad (3-17c)$$

Here, the coefficients $b_{n,m,l}^{(i)}$ specify the expansion of $b_{n,m,l}$ with respect to the shear rate, $\dot{\gamma}$.

From eqs 3-9 and 3-10 combined with eqs 3-14, 3-16, and 3-17, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ are calculated up to the lowest order of nonlinearity. The results can be summarized as

$$\frac{\eta(\dot{\gamma})}{\eta_0} = 1 + \{\tau_0 \dot{\gamma}\}^2 [b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)}] + O(\{\tau_0 \dot{\gamma}\}^4) \quad \text{with } \eta_0 = \nu k_B T \tau_0 \quad (3-18)$$

$$\frac{\Psi_1(\dot{\gamma})}{\Psi_{1,0}} = 1 + \{\tau_0 \dot{\gamma}\}^2 [b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)} + b_{2,0,0}^{(4)} - b_{0,2,0}^{(4)}] + O(\{\tau_0 \dot{\gamma}\}^4) \quad \text{with } \Psi_{1,0} = 2 \nu k_B T \tau_0^2 \quad (3-19)$$

In the linear viscoelastic regime at low $\dot{\gamma}$, the model so far developed (eqs 3-13, 3-14, and 3-15) gives the single-Maxwellian behavior associated with η_0 and $\Psi_{1,0}$ shown in eqs 3-18 and 3-19. In contrast, in the nonlinear regime, $\eta(\dot{\gamma})$ deduced from the model exhibits thickening while $\Psi_1(\dot{\gamma})$ remains close to the linear $\Psi_{1,0}$ if the coefficients satisfy the conditions, $b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)} > 0$ and $b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)} \cong -\{b_{2,0,0}^{(4)} - b_{0,2,0}^{(4)}\}$. Namely, the model incorporating neither the FENE effect nor the shear-induced increase of ν reproduces qualitatively the behavior of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ experimentally observed for the HEUR solution at intermediate $\dot{\gamma}$, given that the expansion coefficients satisfy these conditions.

As can be clearly noted from eqs 3-18 and 3-19, the anisotropy of the orientation of the newly created (associated) strands, represented by the coefficients $b_{n,m,l}$ for $\phi_{ss}(\mathbf{r}, \dot{\gamma})$ (cf. eq 3-15), determines the thickening/thinning behavior of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$. Specifically, the coefficient $b_{n,m,l}$ with $(n,m,l) = (1,1,0)$ corresponds to the mode of strand creation in the direction parallel to $\mathbf{e}_x + \mathbf{e}_y$, where $\mathbf{e}_x$ and $\mathbf{e}_y$ are the unit vectors in the shear and shear gradient direction, respectively. Similarly, the coefficients $b_{n,m,l}$ with $(n,m,l) = (2,0,0)$ and $(0,2,0)$ correspond to the mode of strand creation in the directions parallel to $\mathbf{e}_x$ and $\mathbf{e}_y$, respectively. Thus, if the strands are preferentially created in the shear gradient direction rather than the shear direction and much less favorably in the direction in between (parallel to $\mathbf{e}_x + \mathbf{e}_y$), the $\dot{\gamma}$ -expansion coefficients could have values in the order of $b_{0,2,0}^{(4)} > b_{2,0,0}^{(2)} > b_{2,0,0}^{(4)} > b_{1,1,0}^{(3)} (> 0)$, thereby simultaneously fulfilling the condition for thickening of $\eta(\dot{\gamma})$, $b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)} > 0$, and the condition for the lack of nonlinearity of $\Psi_1(\dot{\gamma})$,

$b_{1,1,0}^{(3)} + 2b_{2,0,0}^{(2)} \cong -\{b_{2,0,0}^{(4)} - b_{0,2,0}^{(4)}\}$. (For $b_{2,0,0}^{(2)}$ and $b_{2,0,0}^{(4)}$ having the same (n,m,l) , the difference due to the expansion order, $b_{2,0,0}^{(2)} > b_{2,0,0}^{(4)}$, has been considered here.) The preferential strand creation in the shear gradient direction appears to be reasonable, because the HEUR micellar cores are distributed anisotropically under shear and the strand is rather stabilized (not significantly stretched) if it is created in this direction, and also because the already existing strands tend to be oriented out of that direction. (It is also worth mentioning that the anisotropy of the molecular mobility has been considered in the constitutive equation⁴⁷ and molecular model⁴⁸. This anisotropy of mobility could also result in the preferential creation of the strands in the shear gradient direction.)

Of course, the above model does not specify the mechanism of the strand creation and the dynamics of the source function $\phi_{ss}(\mathbf{r}, \dot{\gamma})$, and it is too simple to reproduce the experimental results quantitatively. In addition, it does not necessarily apply to all HEUR solutions so far examined in literature: The FENE effect and shear-induced increase of ν could have been important for some solutions. Nevertheless, it should be emphasized that the thickening of $\eta(\dot{\gamma})$ associated with nonlinearity of $\Psi_1(\dot{\gamma})$ observed for our 1.0 wt% HEUR solution at relatively low $\dot{\gamma}$ can be qualitatively explained by the simple transient Gaussian network model considering no FENE effect and no increase of ν . This simple model can be deduced from a more general/complete “sparse network” model formulated in Chapter 4, and thus have a wider applicability than expected from the simple kinetic balance considered therein (eq 3-13).

3-4-3. Mechanism of shear thinning

For the HEUR solution, both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ exhibit thinning at high $\dot{\gamma}$, as noted in Figures 3-3, 3-4, and 3-5. The initial decay of $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ at those $\dot{\gamma}$ is faster than that in the linear regime (Figure 3-7). In addition, the $\dot{\gamma}$ dependence of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ of the HEUR solution is stronger than that for entangled polymers (cf. eqs 3-5 and 3-8). These results suggest that the thinning of the HEUR solutions is attributable to the shear-induced disruption of the HEUR network, i.e., the decrease of the number density ν of the active strands. This point will be further examined in Chapter 6 with the aid of fluorescence measurements for HEUR chains having dye groups at the ends.

Finally, it should be noted that the thinning of $\eta(\dot{\gamma})$ is associated with the transient thickening of $\eta^+(t; \dot{\gamma})$ above the linear $\eta^+(t)$ while the thinning of $\Psi_1(\dot{\gamma})$ is associated with no significant overshoot of $\Psi_1^+(t; \dot{\gamma})$ (very weak overshoot, if any) above the linear $\Psi_1^+(t)$; cf. Figures 3-4 and 3-5. These features of $\eta^+(t; \dot{\gamma})$ and $\Psi_1^+(t; \dot{\gamma})$ appear to correspond to the anisotropic creation of the strands in the transient state, as similar to the anisotropic creation in the steady state in the thickening regime discussed earlier (although the transient hardening of the stretched strand, that could occur in a short time scale before disruption of the HEUR core, might contribute a little to those features). However, the model developed in the previous section cannot apply to those $\eta^+(t; \dot{\gamma})$ and $\Psi_1^+(t; \dot{\gamma})$ data, because changes in the dynamics of the source function with time in the transient state has not been specified within the model (which, however, in turn provides the model with a large generality). A more detailed model explicitly specifying the dynamics of the

source function is required for description of the transient thickening followed by the steady state thinning.

3-5. Conclusions

For the 1.0 wt% aqueous HEUR solution containing the transient network of suberbridge chains and exhibiting the single-Maxwellian relaxation in the linear regime, the nonlinear thickening and thinning behavior under shear flow was extensively examined.

At intermediate shear rates $\dot{\gamma}$ just above the equilibrium relaxation frequency $1/\tau$, the solution exhibited thickening characterized by monotonic increase of the viscosity growth function $\eta^+(t; \dot{\gamma})$ above the linear $\eta^+(t)$ and by the steady state viscosity $\eta(\dot{\gamma})$ larger than η_0 . However, at those $\dot{\gamma}$, the first normal stress coefficient growth function $\Psi_1^+(t; \dot{\gamma})$ and the steady state coefficient $\Psi_1^+(\dot{\gamma})$ exhibited no nonlinearity. In addition, the relaxation times of the viscosity and normal stress coefficient decay functions $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ obtained after cessation of steady flow agreed with those in the linear regime. These results, in particular the lack of nonlinearity of $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$, suggested that the HEUR network strands (superbridges) in the 1.0 wt% solution were just moderately stretched to show no significant FENE effect and that the number density ν of those strands was negligibly affected by the shear at $\dot{\gamma}$ just above $1/\tau$. A simple transient Gaussian network model incorporating neither the FENE effect nor the increase of ν suggested that the thickening of $\eta^+(t; \dot{\gamma})$ and $\eta(\dot{\gamma})$ and the lack of nonlinearity of $\Psi_1^+(t; \dot{\gamma})$ and $\Psi_1^+(\dot{\gamma})$ could mainly reflect the anisotropy of strand creation (reassociation) under shear flow. The strand

creation appeared to be enhanced in the shear gradient direction to result in both thickening of $\eta^+(t; \dot{\gamma})$ and $\eta(\dot{\gamma})$ and lack of nonlinearity of $\Psi_1^+(t; \dot{\gamma})$ and $\Psi_1(\dot{\gamma})$.

In contrast, at $\dot{\gamma} \gg 1/\tau$, $\eta^+(t; \dot{\gamma})$ exhibited overshoot well above the linear $\eta^+(t)$ and then approached $\eta(\dot{\gamma}) < \eta_0$, whereas $\Psi_1^+(t; \dot{\gamma})$ showed no significant overshoot (very weak overshoot, if any) to approach $\Psi_1(\dot{\gamma}) \ll \Psi_{1,0}$. In addition, the relaxation of $\eta^-(t; \dot{\gamma})$ and $\Psi_1^-(t; \dot{\gamma})$ after cessation of flow was considerably faster than that in the linear regime. These nonlinear thinning features at $\dot{\gamma} \gg 1/\tau$ can be mainly attributed to the flow-induced disruption/fragmentation of the HEUR network (decrease of ν).

Appendix 3A. Analysis of elastic energy

It is informative to compare the elastic energy of the HEUR network strands F_{el} and the association energy of the end groups of those strands, $E_a \cong 88 \text{ kJ mol}^{-1}$ (evaluated from the data in Figure 3-2), to test if the association is strong enough to allow the strands to be stretched into the FENE regime. F_{el} increases with increasing end-to-end distance r of the strand. Thus, the end groups can sustain the strand stretching only in a region of r specified by

$$F_{el}(r) < E_a \quad (3A-1)$$

The FENE effect emerges if r in this region can have a value reasonably close to the full-stretch length of the strand, and *vice versa*.

This test can be achieved by utilizing the expression of $F_{el}(r)$ deduced from the standard FENE model³⁸,

$$F_{\text{el}}(r) = -\frac{3n_K RT}{2} \ln \left[1 - \frac{r^2}{(n_K b_K)^2} \right] \quad \text{per 1 mole of strands} \quad (3A-2)$$

Here, n_K is the number of Kuhn segments per strand, b_K is the Kuhn step length, and the product $n_K b_K$ corresponds to the full-stretch length of the strand. The ratio $\lambda_f = r/n_K b_K$ (a factor governing the r dependence of F_{el} in eq A3-2) specifies the relative stretch of the strand with respect to the full-stretch limit. Because $F_{\text{el}}(r)$ for a given λ_f value increases with increasing n_K , eq 3A-1 can be satisfied in a wider range of λ_f to allow the FENE effect to emerge more easily for a smaller n_K value. Thus, eq 3A-1 can be most critically tested for an unrealistically small (nominally minimum) n_K value, $n_K = 511$ for individual HEUR chains: This n_K value was obtained from the b_K data of PEO⁴⁹, $b_K = 0.77$ nm, and $M_w (= 4.6 \times 10^4)$ of the HEUR chain. The actual HEUR network strand is a superbridge (connected sequence of HEUR chains) as explained for eq 3-2, and the actual n_K value should be much larger than 511. Thus, the actual HEUR strand can exhibit the FENE effect much *less easily* compared to the extreme case examined below.

For the values $n_K = 511$, $b_K = 0.77$ nm, and $E_a = 88$ kJ mol⁻¹, eq A3-2 specifies the range of λ_f (range of r) where eq A1 is satisfied. The result is

$$\lambda_f < \left[1 - \exp \left(-\frac{2}{3n_K RT} E_a \right) \right]^{1/2} = 0.21 \quad (\text{at } 25^\circ\text{C}) \quad (3A-3)$$

The maximum possible λ_f value, 0.21, is still too small to allow a significant FENE effect to emerge for the elasticity of the HEUR chain, as can be clearly noted from comparison between the FENE energy $F_{\text{el}}(\lambda_f) = 85.6$ kJ mol⁻¹ (eq 3A-2) and the Gaussian elastic energy, $F_{\text{el,G}}(\lambda_f) = \{3n_K RT/2\} \lambda_f^2$ E 85.2 kJ mol⁻¹. The close coincidence of $F_{\text{el}}(\lambda_f)$ and $F_{\text{el,G}}(\lambda_f)$ indicates that the FENE feature cannot significantly emerge for $\lambda_f = 0.21$. (The FENE feature can be prominent only when

$$F_{el}(\lambda_f) \gg F_{el,G}(\lambda_f).$$

The actual HEUR strands exhibits the FENE effect much less easily compared to individual HEUR chains examined above. Thus, this effect should have a negligible contribution to the actual HEUR solution, and the HEUR strands can be safely regarded as the Gaussian strands.

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Chapter 4: Concentration Dependence of Linear Viscoelasticity of HEUR Aqueous Solutions

4-1. Introduction

In Chapter 3, the HEUR aqueous solutions were found to exhibit nonlinear shear thickening and thinning. As discussed in Chapter 3, one possible origin of the shear thickening is the anisotropy of the reassociation dynamics under shear flow. Although the anisotropy reasonably explains the experimentally observed thickening and thinning behavior of the shear viscosity and the first normal stress difference data, several problems still remain. For example, it was not clear what the network structure of the HEUR chains is, how the chains generate the stress, and how the reassociation of chain ends can be anisotropic. It was also unclear whether the mean-field single-chain type model, which was employed in Chapter 3, is justified from the molecular (microscopic) point of view or not. To answer these problems, it is necessary to focus on a relatively small (microscopic) scale and re-examine the structure and dynamics of HEUR chains in that scale.

Prior to analysis of the nonlinear rheological properties, the linear rheological properties should be considered carefully. It should be noted that the linear viscoelasticity of HEUR solutions is not so simple. One example is found for the concentration dependence of the linear viscoelasticity. The simple transient network type models^{1,2} (such as the Tanaka-Edwards model) give simple concentration dependence for rheological properties. Namely, the relaxation time τ is independent of the HEUR concentration c , and the characteristic modulus G_0 is proportional to the chain number density and thus is simply proportional to c . Correspondingly, the storage and loss moduli exhibit

the c -independent universal relaxation mode distribution, typically of the single Maxwellian form. These naive expectations from the simple transient network type models are, however, qualitatively not consistent with experimental data. Annable et al³ studied the concentration dependence of HEUR solutions in detail, and found some nontrivial behavior. Their data clearly show that τ and G_0 depend on c rather strongly, and the storage and loss moduli do not relax in the single Maxwellian form in particular at relatively high c . In addition, the time-temperature superposition is not perfectly valid at relatively low c , as noted in Chapter 3.

In this chapter, the c dependence of HEUR aqueous solutions is examined in detail on the basis of those linear viscoelastic features. At first, the linear viscoelasticity of the HEUR aqueous solutions with different c (= 1-10 wt%) are measured systematically to analyze the c dependence of several rheological properties, and the structure and dynamics of networks in the HEUR solutions are discussed. Specifically, the sparseness of the network, overlooked in previous transient network type models, is shown to be important. Then, the transient network type models for sparse and dense networks are formulated. By combining the experimental data and theoretical considerations, the c dependence of the properties of the HEUR solutions is related to the sparseness of the network. The nonlinear rheological properties can be analyzed by the same model, and the results will be presented in Chapter 5.

4-2. Experimental

The HEUR with end-hexadecyl groups, being synthesized in Chapter 2, was utilized. The

HEUR aqueous solutions with different HEUR concentrations c ($= 1-10$ wt%) were prepared by dissolving the HEUR into distilled water. Prescribed masses of HEUR and water were stirred for 24 hours to obtain homogeneous HEUR solutions. For comparison, the aqueous solutions of the precursor PEO (without the hydrophobic end groups) were also prepared with the same method.

The linear viscoelasticity measurements were performed with an MCR-301 rheometer (Anton Paar), with a cone-plate type fixture with the diameter $d = 75\text{mm}$ and the cone angle $\theta = 1^\circ$. The storage and loss moduli (G' and G'') were measured at angular frequencies ω ranging from 0.03 rad s^{-1} to 500 rad s^{-1} . The measurements were performed at several different temperatures ($T = 5, 10, 15, 20, \text{ and } 25^\circ\text{C}$) to construct the master curves by using the time-temperature superposition. For the PEO solutions, the linear viscoelasticity could be accurately measured only in a limited range of ω ($= 1-10 \text{ rad s}^{-1}$) due to their low viscosities. Therefore, for the PEO solutions, only the loss modulus data in that range of ω were used.

4-3. Results

It would be informative to start from the 1wt% HEUR aqueous solution, which was studied in Chapter 3. In Chapter 3, a master curve for the 1wt% HEUR solution was constructed, by applying the time-temperature superposition for the low angular frequency region. The master curve including the high ω data is shown in Figure 4-1. As before, the time-temperature superposition works well at low ω and the storage and loss moduli in the terminal regime can be fitted well by the single Maxwellian forms, $G'(\omega) = G_0 \tau^2 \omega^2 / [1 + \tau^2 \omega^2]$ and $G''(\omega) = G_0 \tau \omega / [1 + \tau^2 \omega^2]$, with G_0 and τ

being the characteristic modulus and the relaxation time, respectively. However, the superposition at high ω fails, which implies the existence of another relaxation mode with a short relaxation time. If such a mode exists, the time-temperature superposition at high ω would be possible by the use of another horizontal shift factor.

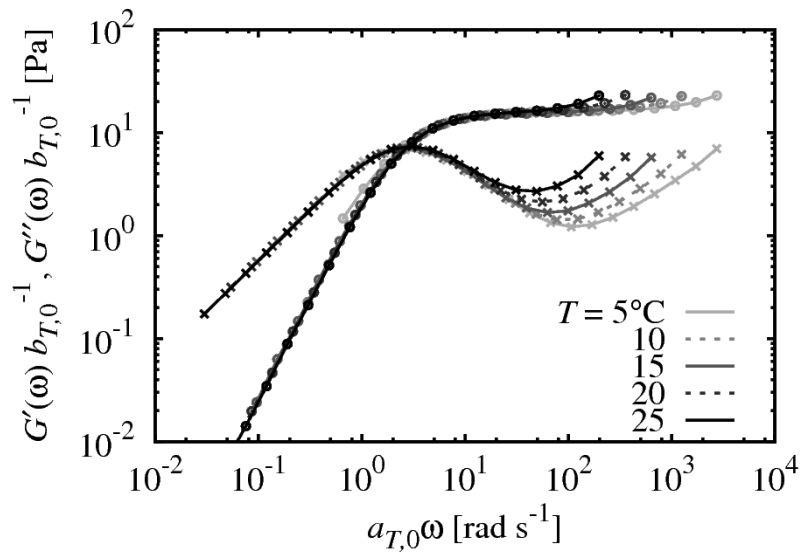


Figure 4-1: A master curve for the storage and loss moduli of the 1wt% HEUR aqueous solution, for the low angular frequency region (the reference temperature is $T_r = 25^\circ\text{C}$).

Because the fast mode is considered to originate from a structure smaller than the HEUR network, it would be reasonable to relate this mode to the linear viscoelasticity of the PEO aqueous solutions. To verify this expectation, another set of master curves was constructed by using the horizontal and vertical shift factors for the PEO solution. The resulting master curves are shown in Figure 4-2, together with the loss modulus of the PEO solution at $T=25^\circ\text{C}$. In this case, the time-temperature superposition reasonably holds at high ω . It would be worth mentioning here that the horizontal shift factor used for the master curves of the fast mode has almost the same temperature dependence

as the viscosity of water.⁴⁾ This is reasonable because the Zimm model⁵ predicts that the relaxation time is proportional to the viscosity of the medium (in this case, the viscosity of water).

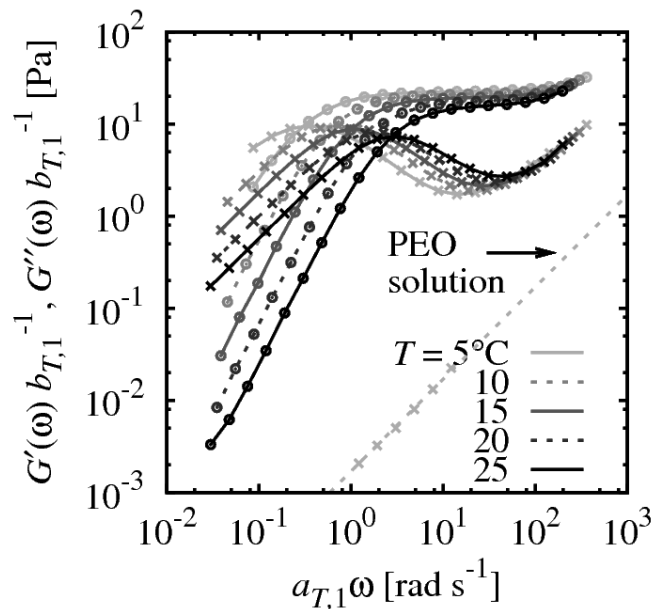


Figure 4-2: A master curve for the storage and loss moduli of the 1wt% HEUR aqueous solution at high angular frequency region (the reference temperature is $T_r = 25^\circ\text{C}$).

$a_{T,1}$ and $b_{T,1}$ are the horizontal and vertical shift factors of the reference PEO solution.

From these experimental data, it would be reasonable to consider the existence of two different relaxation modes, referred to as the “slow” and “fast” modes, in the HEUR aqueous solution. The horizontal shift factors, $a_{T,0}$ and $a_{T,1}$, for the slow and fast modes are shown in Figure 4-3. Both factors obey the Arrhenius law but the activation energies are different. The slow mode clearly corresponds to the relaxation of the HEUR network through the reassociation of hydrophobic chain ends. On the other hand, the origin of the fast mode remained unclear. Ng et al⁶ proposed that the fast mode is attributable to the relaxation of the micellar cores. In contrast, Bedrov et al⁷ proposed that the fast mode is the local relaxation mode of the PEO chains. As shown in Figure 4-2, the fast

mode has the same horizontal and vertical shift factors as the PEO solution, and thus the interpretation by Bedrov et al⁷ seems to be reasonable.

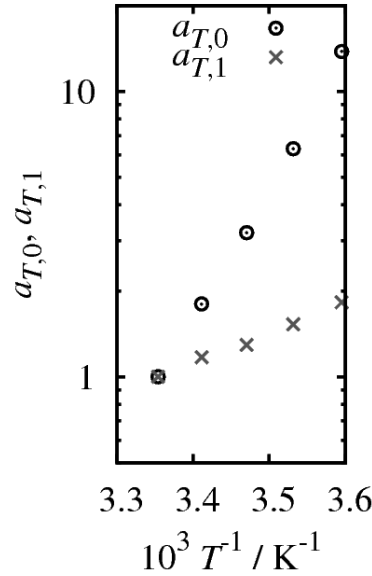


Figure 4-3: Horizontal shift factors for the master curves for the 1wt% HEUR aqueous solution. $a_{T,0}$ and $a_{T,1}$

If the fast mode reflects the local motion of the PEO chains, that mode is expected to strongly depend on the change of the environment for the PEO chains, that is, change of the concentration c . Figure 4-4 shows the storage and loss moduli of HEUR solutions with different c (= 1, 2, 5, and 10 wt%) at $T = 25^\circ\text{C}$. Clearly, the ω dependence of the storage and loss moduli at high ω largely changes with c . This result is consistent with the above expectation, and thus the fast mode is surely attributed to the local relaxation mode of the PEO chains.

Figure 4-4 also shows that the ω dependence of the storage and loss moduli at low ω reflecting the slow mode is not so sensitive to c . For a further test of this ω dependence, Figure 4-5 shows plots of the storage and loss moduli normalized by the characteristic modulus G_0 against the normalized angular frequency, $\tau\omega$. Interestingly, the normalized storage and loss moduli do not

collapse into the Maxwellian form. At low c , the storage and loss moduli can be fitted reasonably well by the single Maxwellian form, except at high ω where the fast mode becomes dominant. In contrast, at high c , the moduli cannot be fitted by the single Maxwellian form even at low ω , and their relaxation broadens with increasing c . Similar behavior has been reported for some HEUR solutions by Annable et al.³ Furthermore, S      et al.^{8,9} reported that the relaxation modulus $G(t)$ can be fitted well by the stretched exponential, $G(t) = G_0 \exp[-(t/\tau)^\alpha]$ (with G_0 , τ , and α being the fitting parameters) instead of the single Maxwellian form. The deviation from the single Maxwellian form may reflect the structural change of the HEUR network in the solutions.

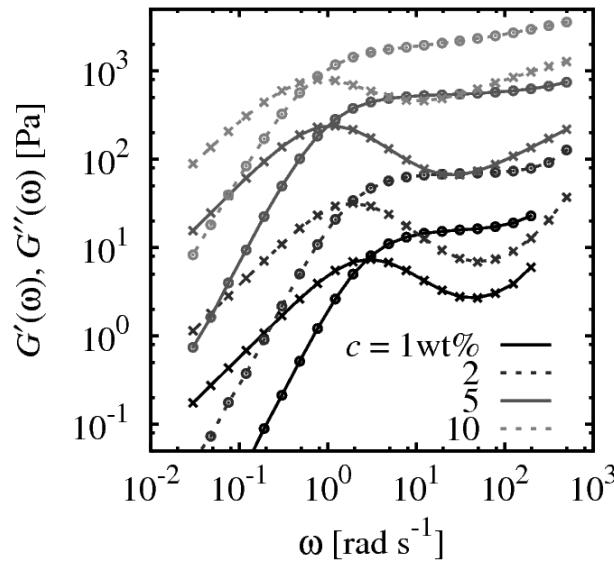


Figure 4-4: Storage and loss moduli of HEUR aqueous solutions with different concentrations at $T=25^\circ\text{C}$.

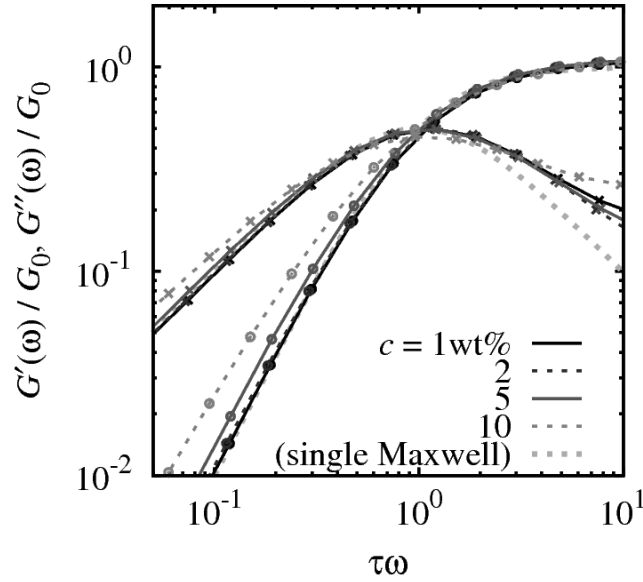


Figure 4-5: Storage and loss moduli of HEUR aqueous solutions with different concentrations at $T=25^{\circ}\text{C}$, rescaled by the characteristic modulus G_0 and the relaxation time τ .

If the network structure changes with c , the rheological properties should also change (and the simple transient network type models fails, as explained earlier). Thus, it is informative to examine the c dependence of the relaxation time τ and the characteristic modulus G_0 . As shown in Figure 4-6, both τ and G_0 strongly depend on the c , and their c dependence changes at a critical concentration $c_c \approx 4\text{wt}\%$. Specifically, τ and G_0 can be fitted with power-law type relations with different exponents at low and high c (shown with the dotted and solid lines in Figure 4-6):

$$\tau \propto c^{0.63} \quad (c < 4 \text{ wt}\%), \quad \tau \propto c^{0.32} \quad (c > 4 \text{ wt}\%) \quad (4-1)$$

$$G_0 \propto c^{2.3} \quad (c < 4 \text{ wt}\%), \quad G_0 \propto c^{1.8} \quad (c > 4 \text{ wt}\%) \quad (4-2)$$

The ω dependence of the storage and loss moduli also changes at this c_c , as noted in Figure 4-5.

These results strongly suggest that the HEUR network structure changes at c_c .

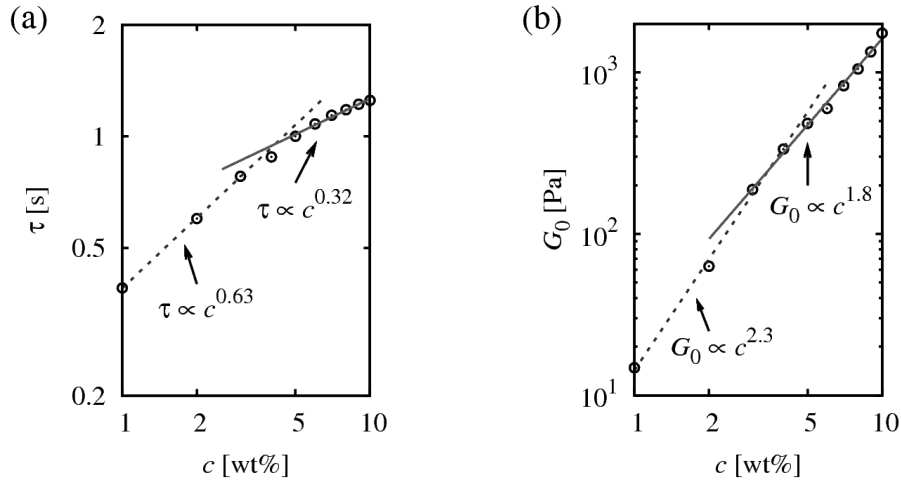


Figure 4-6: The HEUR concentration dependence of (a) the relaxation time and (b) the characteristic modulus.

4-4. Theoretical Model¹⁰

4-4-1. Sparse and Dense Networks

The structural change of the HEUR network discussed above needs to be incorporated into the theoretical models such as the transient network model. At low c , the networks are expected to be “sparse”, and many of micellar cores would have a few bridge chains. In such a situation, the superbridges (connected sequences of chains) should be considered as elastically active chains, instead of the single-chain bridges. Thus the sparse network can be modelled as a network mainly consisting of superbridges, superloops, dangling ends, and loops, as depicted in Figure 4-7. In contrast, at high c , the networks are expected to be “dense”, and many micellar cores would have relatively large numbers of bridge chains, unlike the sparse network case. Then, the dense network can be modelled as a network which mainly consisting of single-chain bridges and loops, as illustrated in Figure 4-8.

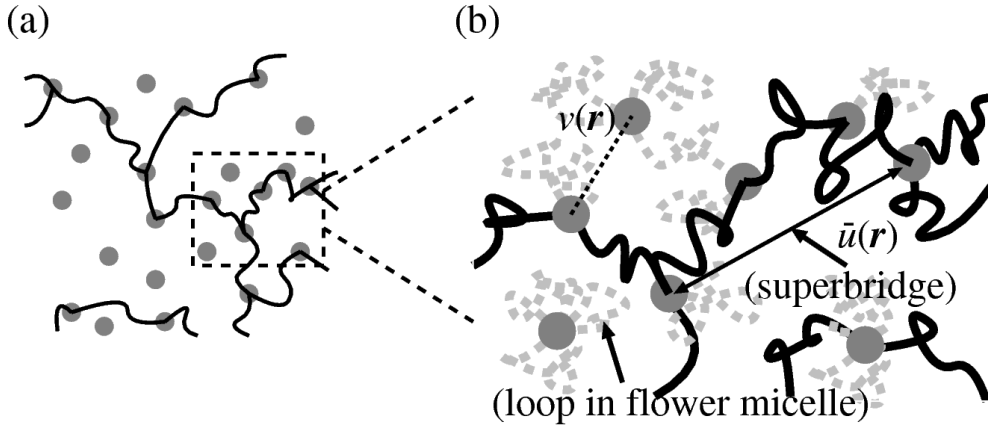


Figure 4-7: Images of the sparse network in a HEUR aqueous solution. (a) large scale and (b) detailed images. Grey circles, black solid curves, and grey dashed curves represents the micellar cores, elastically active bonds (superbridges), and elastically inactive bonds, respectively.

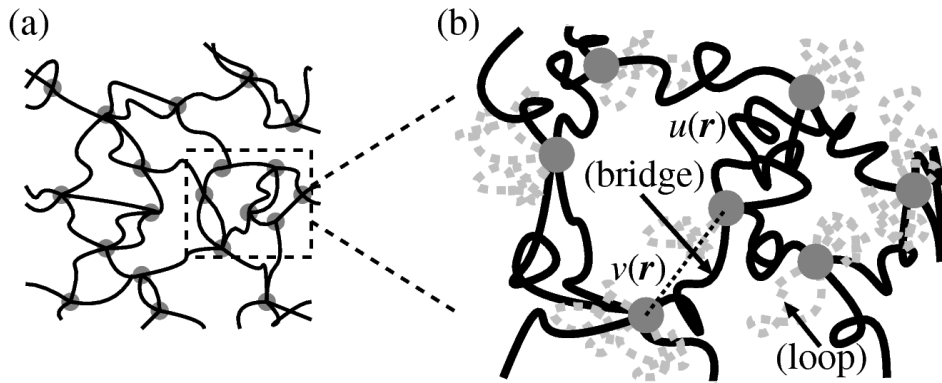


Figure 4-8: Images of the dense network in a HEUR aqueous solution. (a) large scale and (b) detailed images. Grey circles, black solid curves, and grey dashed curves represent the micellar cores, bridge chains, and loop chains, respectively.

According to the above argument, it would be reasonable to formulate the transient network type models for the sparse and dense networks separately. Before detailed modeling, it would be fair to refer to the statistical model by Annable et al³. They considered a simple statistical model which counts the weights of the bridge, loop, superbridge, superloops, and dangling ends. Their model predicts rather strong c dependence of the characteristic modulus and the relaxation time. Although their model was not formulated for calculation of the relaxation modulus (relaxation mode

distribution), it clearly shows the importance of the superstructures.

As discussed in Chapter 3, it would be reasonable to ignore the dangling chains in the modulus calculation and consider the transition dynamics between elastically active and inactive bonds. In the case of the dense network, the bridge and loop are elastically active and inactive bonds, respectively. This seems to be consistent with widely accepted cartoon and is intuitive. In the case of the sparse network, only the superbridges are elastically active bonds, and the loops, superloops, and dangling ends are elastically inactive. Therefore, several different transitions are possible in the sparse network. Single-chain mean-field type transient network models can be formulated for both sparse and dense networks, by considering the appropriate transition processes. This formulation is explained below.

4-4-2. Transient Network Model for Dense Network

The situation is simpler for the dense network than for the sparse network, because the former type of network includes transition just between single-chain bridges and loops. Therefore, it would be better to start the modeling for the dense networks. The schematic image of the dense network is depicted in Figure 4-8. The dense network consists of the bridge and loop chains, and the micellar cores behave as network junctions. The spatial distribution of the micellar core should be coupled with the transition dynamics for the bridge and loop chains. Then, the structure of the dense HEUR network depends on the fractions of bridges and loops, and the spatial distribution of micellar cores. Consequently, the dynamics can be modeled as the dynamical processes for the transitions and the

time-evolution of micellar core distribution.

These physical arguments lead to a set of dynamic equations for several probability distribution functions, in a similar way similar to the conventional transient network type models. To describe the dynamics of the dense network, three distribution functions are required: two distribution functions for the loop and bridge chains, and one spatial distribution function for the micellar cores. In what follows, the loop and bridge are indexed by 0 and 1, respectively, and their distribution functions are expressed as $P(0)$ and $P(1, \mathbf{r})$ ($\mathbf{r}$ is the end-to-end vector of a HEUR chain). (Only the bridge chain has the degrees of freedom of the end-to-end vector.) The pair correlation function $\Phi(\mathbf{r})$, with $\mathbf{r}$ being the spatial distance between two micellar cores, will be suitable to describe the micellar core distribution. Before constructing the dynamical equations, the equilibrium distribution should be specified. The equilibrium distributions for the loop and bridge can be specified as

$$P_{eq}(0) = \frac{1}{\Xi} Z_0 \quad (4-3)$$

$$P_{eq}(1, \mathbf{r}) = \frac{Q_1}{\Xi \Lambda^3} \exp \left[-\frac{v(\mathbf{r}) + u(\mathbf{r})}{k_B T} \right] \quad (4-4)$$

Here Λ is the thermal de Broglie wave length, Z_0 and Q_1 are the partition function of a single loop chain and of a single bridge chain, respectively, Ξ is the full partition function, and $u(\mathbf{r})$ and $v(\mathbf{r})$ are the bond potential and the effective pair interaction potential between micellar cores, respectively.

The two single-chain partition functions are related to each other as

$$\Xi = Z_0 + \frac{Q_1}{\Lambda^3} \int d\mathbf{r} \exp \left[-\frac{v(\mathbf{r}) + u(\mathbf{r})}{k_B T} \right] \quad (4-5)$$

Within the mean-field approximation, the equilibrium pair correlation is simply expressed as

$$v(\mathbf{r}) = -k_B T \ln g_{eq}(\mathbf{r}) + k_B T \ln[1 + \xi e^{-u(\mathbf{r})/k_B T}] \quad (4-6)$$

Here, $g_{eq}(\mathbf{r})$ is the equilibrium radial distribution function (RDF), and $\xi = n_0 Q_1 / \rho_0 \Lambda^3 Z_0$ is the effective fugacity with n_0 being the average number of chain ends per micellar core and ρ_0 , the average micellar core density. The equilibrium micellar core distribution function is specified as

$$\Phi_{eq}(\mathbf{r}) = \frac{\rho_0}{n_0} e^{-v(\mathbf{r})/k_B T} \quad (4-7)$$

The dynamic model should reproduce these equilibrium distributions after full relaxation over a sufficiently long time in the absence of the external deformation.

The simplest dynamics model can be formulated as follows. The bridge-to-loop transition occurs at a certain transition rate¹¹, which may depend on the end-to-end vector of the bridge, $\mathbf{r}$. This can be expressed by the following transition rate.

$$W(0|1, \mathbf{r}) = 1/\tau(\mathbf{r}) \quad (4-8)$$

The loop-to-bridge transition is determined automatically from the detailed balance condition. The explicit form of the transition rate is found to be

$$W(1, \mathbf{r} | 0) = \frac{1}{\tau(\mathbf{r})} \xi e^{-u(\mathbf{r})/k_B T} \quad (4-9)$$

The effect of the Brownian motion should be also considered. It can be expressed by the Fokker-Planck operator¹¹). The Fokker-Planck operator under the mean-field approximation can be expressed in terms of the effective interaction potential between micellar cores, $v(\mathbf{r})$, as

$$L(n)P = \frac{1}{\zeta_0} \frac{\partial}{\partial \mathbf{r}} \left[\frac{\partial[nu + v]}{\partial \mathbf{r}} P + k_B T \frac{\partial P}{\partial \mathbf{r}} \right] - \frac{\partial}{\partial \mathbf{r}} [\mathbf{\kappa} \cdot \mathbf{r} P] \quad (4-10)$$

where ζ_0 is the friction coefficient of the micellar core and $\mathbf{\kappa}$ is the velocity gradient tensor. From the transition rates and the Fokker-Planck operator, the master equations can be constructed

straightforwardly.

$$\frac{\partial P(1, \mathbf{r}, t)}{\partial t} = L(1)P(1, \mathbf{r}) + W(1, \mathbf{r} | 0)\Phi(\mathbf{r})P(0) - W(0 | 1, \mathbf{r})P(1, \mathbf{r}) \quad (4-11)$$

$$\frac{\partial P(0, t)}{\partial t} = \int d\mathbf{r} [W(0 | 1, \mathbf{r})P(1, \mathbf{r}) - W(1, \mathbf{r} | 0)\Phi(\mathbf{r})P(0)] \quad (4-12)$$

Here, it should be emphasized that the distribution function of micellar cores is directly coupled to the dynamic equations for the loop and bridge chains. To make the closed set of dynamic equations, the dynamic equation for the micellar cores is required. For the dynamic equation of the micellar cores, the Fokker-Planck equation will be suitable. Under the mean-field approximation, the Fokker-Planck equation can be expressed as

$$\frac{\partial \Phi(\mathbf{r}, t)}{\partial t} = L(0)\Phi(\mathbf{r}) \quad (4-13)$$

The above set of three dynamic equations describes the time-evolution of the loop and bridge chains and the micellar core distribution. In the dense network model, the properties of the dense network are expected to depend strongly on the micellar core distribution. The micellar core distribution in turn depends strongly on the concentration, and thus the dense network model naturally predicts the strong concentration dependence of the linear rheological properties. The linear viscoelasticity will be calculated in Section 4-4-4.

4-4-3. Transient Network Model for Sparse Network

Differing from the dense network, the sparse network mainly consists of superstructures such as the superbridges. Only the superbridges are elastically active, and thus the transition from and to the superbridge becomes essential. In this sense, the details of elastically inactive structures (loops,

superloops, and dangling ends) are not important, and they can be modelled as elastically inactive, effective loops, as illustrated in Figure 4-7. From this consideration, it will be sufficient to consider the transition between elastically active and inactive effective bonds, and such a transition process can be modeled in a way similar to the dense network case. The distribution functions for the inactive and active effective bonds are expressed as $\bar{P}(0)$ and $\bar{P}(1, \mathbf{r})$.

The equilibrium distribution for the inactive bond can be expressed in a way similar to the case of the dense network model.

$$\bar{P}_{eq}(0) = \frac{1}{\bar{\Xi}} \bar{Z}_0 \quad (4-14)$$

$$\bar{P}_{eq}(1, \mathbf{r}) = \frac{\bar{Q}_1}{\bar{\Xi} \Lambda^3} \exp \left[-\frac{\bar{v}(\mathbf{r}) + \bar{u}(\mathbf{r})}{k_B T} \right] \quad (4-15)$$

Here, $\bar{Z}_0$ is the partition function for the inactive bond (that is, the partition function for loops, superloops, and dangling ends), and $\bar{\Xi}$ is the full partition function. $\bar{u}$ and $\bar{v}$ are effective potentials defined in a way similar to the case of the dense network model, except that an active bond (superbridge) consists of multiple chains.

The equilibrium distribution for the active bond is not that simple. Because a superbridge consists of multiple chains, an approximate expression can be obtained by combining the distribution function for the single-chain bridge and micellar cores. It reads

$$\bar{P}_{eq}(1, \mathbf{r}) \propto \bar{P}_{eq}^{[m]}(1, \mathbf{r}) \quad (4-16)$$

where a short-hand notation for multiple convolutions has been introduced:

$$f^{[m]}(\mathbf{r}) = f * f * \dots * f \quad (m \text{ convolutions}) \quad (4-17)$$

Then, the effective bond potential $\bar{u}$ can be related to the potentials u and v as

$$\bar{u}(\mathbf{r}) = -v(\mathbf{r}) - k_B T \ln \left[\Lambda^{-3(m-1)} [e^{-(u+v)/k_B T}]^{[m]}(\mathbf{r}) \right] \quad (4-18)$$

The transition rates can be modelled similarly. The transition from active to inactive bonds is contributed from all the bridge chains in a superbridge. Thus, if there are m bridges in a superbridge, the transition rate can be simply expressed as

$$W(0|1, \mathbf{r}) = m/\tau(\mathbf{r}) \quad (4-19)$$

The number of bridges m should be considered as an average for all superbridges, and this m increases as the chain concentration decreases and the functionality decreases. The inactive to active transition rate is determined by the detailed balance condition.

$$W(1, \mathbf{r} | 0) = \frac{m}{\tau(\mathbf{r})} \bar{\xi} e^{-\bar{u}(\mathbf{r})/k_B T} \quad (4-20)$$

Here, $\bar{\xi}$ is the effective fugacity. From this form, the linear rheological properties of the sparse network model are expected to be qualitatively different from those of the dense network model.

The dynamic equations for the active and inactive bonds are expressed as

$$\frac{\partial \bar{P}(1, \mathbf{r}, t)}{\partial t} = \bar{L}(1) \bar{P}(1, \mathbf{r}) + \bar{W}(1, \mathbf{r} | 0) \tilde{\Phi}^{[m]}(\mathbf{r}) \bar{P}(0) - \bar{W}(0 | 1, \mathbf{r}) \bar{P}(1, \mathbf{r}) \quad (4-21)$$

$$\frac{\partial \bar{P}(0, t)}{\partial t} = \int d\mathbf{r} [\bar{W}(0 | 1, \mathbf{r}) \bar{P}(1, \mathbf{r}) - \bar{W}(1, \mathbf{r} | 0) \tilde{\Phi}^{[m]}(\mathbf{r}) \bar{P}(0)] \quad (4-22)$$

where $\bar{L}(n)$ is the Fokker-Planck operator (defined similarly to the case of dense network).

$\tilde{\Phi}^{[m]}(\mathbf{r})$ is the multiple convolution with weight functions defined as

$$\tilde{\Phi}^{[m]}(\mathbf{r}) = \frac{e^{[\bar{v}(\mathbf{r}) - v(\mathbf{r})]/k_B T}}{\Lambda^{3(m-1)}} \sum_k \left[(e^{-u/k_B T} \Phi)^{[m-k]} * \Phi * (e^{-u/k_B T} \Phi)^{[k]} \right] \quad (4-23)$$

These equations are formally similar to those for the sparse network case, but the multiple convolution of the micellar cores (eq 4-23) makes the $\mathbf{r}$ dependence much more complicated. The structure and dynamics of the micellar cores are considered not to be much different from the dense

network case. Thus, it seems reasonable to simply assume that the equilibrium structure and the dynamic equation for the micellar core distribution are common for the dense and sparse network cases. The dynamic equations for the inactive and active bonds together with one for the micellar cores make the closed set of equations that enables calculation of the rheological properties of the sparse network model.

4-4-4. Concentration Dependence of Linear Viscoelasticity

The dense and sparse network models shown in the previous subsections can be utilized to calculate various rheological properties. Here, the linear viscoelasticity is calculated at first for these models with some harmless approximations, and the concentration dependence of the linear viscoelastic properties is discussed.

To calculate the rheological properties, the explicit expression for the stress tensor is required.

One possible form is the Kramers expression,

$$\boldsymbol{\sigma}(\mathbf{r}) = \frac{n_0 \rho_0 k_B T}{2} \int d\mathbf{r} \frac{\partial u(\mathbf{r})}{\partial \mathbf{r}} \mathbf{r} P(1, r) \quad (\text{for dense network}) \quad (4-24a)$$

$$\boldsymbol{\sigma}(\mathbf{r}) = \bar{n}_{eff} \rho_0 k_B T \int d\mathbf{r} \frac{\partial \bar{u}(\mathbf{r})}{\partial \mathbf{r}} \mathbf{r} P(1, r) \quad (\text{for sparse network}) \quad (4-24b)$$

with $\bar{n}_{eff}$ being the number of active chains per micellar core. In eq 4-24, only the stress due to elastically active chains has been considered (and the interaction between micellar cores is approximated to have no contribution to the stress).

To perform explicit calculation, some simplifications and/or approximations should be introduced.

Here, two approximations are introduced.

$$\tau(\mathbf{r}) = \tau_0 \quad (4-25)$$

$$u(\mathbf{r}) = \frac{3k_B T}{2R_0^2} \mathbf{r}^2 \quad (\text{for dense network}), \quad \bar{u}(\mathbf{r}) = \frac{3k_B T}{2mR_0^2} \mathbf{r}^2 \quad (\text{for sparse network}) \quad (4-26)$$

Equations 4-25 and 4-26, respectively, assume the stretch-independent dissociation rate and the ideal Gaussian conformation of the chain. These assumptions sound physically plausible in usual experimental conditions where the shear is rather slow and the chains are subjected to no finite extensible nonlinear elasticity (FENE) effect. With these approximations, the models become simpler and the linear viscoelasticity can be easily calculated.

It would be reasonable to start from the dense network model, which has a simpler mathematical structure. The shear relaxation modulus can be calculated as the response of the stress to a small step strain γ applied to the system. This can be realized by using the equilibrium distributions as the initial distributions at $t = 0$, and setting the Fokker-Planck operator as

$$L(n)P = L_0 P - \gamma \delta(t) \frac{\partial}{\partial r_x} [r_y P] \quad (4-27)$$

Here, L_0 is the equilibrium Fokker-Planck operator, and the small step strain γ is regarded as a perturbation parameter. The distribution functions can be then expanded into a power-law series of γ , and the higher order terms are truncated in the calculation of the linear response.

The micellar core distribution and the loop distribution can be calculated as

$$\Phi(\mathbf{r}, t) = \Phi_{eq}(\mathbf{r}) + \frac{\gamma}{k_B T} e^{tL_0(0)} \left[\frac{\partial \nu(\mathbf{r})}{\partial r_x} r_y \Phi_{eq}(\mathbf{r}) \right] \quad (4-28)$$

$$P(0, t) = P_{eq}(0) \quad (4-29)$$

and the bridge distribution, as

$$\begin{aligned}
P(\mathbf{l}, \mathbf{r}, t) = & P_{eq}(\mathbf{l}, \mathbf{r}) + \frac{\gamma}{k_B T} e^{t[L_0(1)-1/\tau_0]} \left[\left[\frac{3k_B T r_x}{R_0^2} + \frac{\partial v(\mathbf{r})}{\partial r_x} \right] r_y P_{eq}(\mathbf{l}, \mathbf{r}) \right] \\
& + \frac{\gamma \xi P_{eq}(0)}{k_B T} \int_0^t dt' e^{(t-t')[L_0(1)-1/\tau_0]} \left[e^{-3\mathbf{r}^2/2R_0^2} e^{t'L_0(0)} \frac{\partial v(\mathbf{r})}{\partial r_x} r_y \Phi_{eq}(\mathbf{r}) \right] \quad (4-30)
\end{aligned}$$

From the stress tensor and the bridge distribution, the shear relaxation modulus is calculated straightforwardly. The result is

$$\begin{aligned}
G(t) = & \frac{n_0 \rho_0}{2} \left[\int d\mathbf{r} \frac{3r_x r_y}{k_B T} e^{t[L_0(1)-1/\tau_0]} \left[\left[\frac{3k_B T r_x}{R_0^2} + \frac{\partial v(\mathbf{r})}{\partial r_x} \right] r_y P_{eq}(\mathbf{l}, \mathbf{r}) \right] \right. \\
& \left. + \frac{\xi P_{eq}(0)}{\tau_0} \int_0^t dt' e^{(t-t')[L_0(1)-1/\tau_0]} \left[e^{-3\mathbf{r}^2/2R_0^2} e^{t'L_0(0)} \frac{\partial v(\mathbf{r})}{\partial r_x} r_y \Phi_{eq}(\mathbf{r}) \right] \right] \quad (4-31)
\end{aligned}$$

Equation (4-31) includes two different terms contributing to the shear relaxation modulus. Thus, the relaxation deduced from the dense network model does not agree with the single Maxwellian form.

For the sparse network case, the relaxation modulus can be calculated in a similar way, but some additional simplifications are possible. Because the sparse network is formed by superbridges, the dynamics of micellar cores will negligibly contribute to the stress. Then, the Fokker-Planck operator may be simplified as

$$\bar{L}(n)P \approx -\gamma \delta(t) \frac{\partial}{\partial r_x} [r_y P] \quad (4-32)$$

and the shear relaxation modulus becomes

$$G(t) \approx \bar{n}_{eff} \rho_0 k_B T \int d\mathbf{r} \frac{3r_x r_y^2}{m R_0^2} \left[\frac{3r_x}{m R_0^2} + \frac{\partial v(\mathbf{r})}{\partial r_x} \right] \bar{P}_{eq}(\mathbf{l}, \mathbf{r}) e^{-mt/\tau_0} \quad (4-33)$$

This is of a single exponential form having the relaxation time τ_0 , and thus the relaxation of the sparse network is expressed in the single Maxwellian form.

4-5. Discussion

4-5-1. Storage and Loss Moduli

As shown in Section 4-4-4, the shear relaxation modulus $G(t)$ of the dense network model deviates from the single Maxwellian form. Unfortunately, the expression for the shear relaxation modulus is still complicated, and discussion of its non-Maxwellian form requires further simplification for the dense network model. One useful approximation is to replace the Fokker-Planck operator by its characteristic eigenvalue, $L(n) \approx -1/\tau_n$. With this approximation, $G(t)$ is simplified as

$$G(t) \approx G_0 e^{-t[1/\tilde{\tau}(0)+1/\tau_0]} + G_1 \frac{e^{-t/\tilde{\tau}(0)} - e^{-t[1/\tilde{\tau}(1)-1/\tau_0]}}{1 + \tau_0/\tilde{\tau}(1) - \tau_0/\tilde{\tau}(0)} \quad (4-34)$$

where G_0 and G_1 are defined by

$$G_0 = \frac{n_0 \rho_0}{2} \int d\mathbf{r} \frac{3r_x r_y^2}{R_0^2} \left[\frac{3k_B T r_x}{R_0^2} + \frac{\partial v(\mathbf{r})}{\partial r_x} \right] \quad (4-35)$$

$$G_1 = \frac{n_0 \rho_0 \xi P_{eq}(0)}{2} \int d\mathbf{r} \frac{3k_B T r_x r_y^2}{R_0^2} \frac{\partial v(\mathbf{r})}{\partial r_x} e^{-3r^2/2R_0^2} \Phi_{eq}(\mathbf{r}) \quad (4-36)$$

Figure 4-9 shows the storage and loss moduli calculated from the dense network model (eq 4-34).

As the G_1/G_0 ratio increases, the storage and loss moduli deviate from the single Maxwellian form. Because G_1 becomes relatively large when the network functionality is large and/or the correlation between micellar cores is strong, such large G_1/G_0 ratio can naturally emerge in high concentration HEUR solutions. In the sparse network model, as shown in eq (4-33), the shear relaxation modulus reduces to the single Maxwellian form. This result is qualitatively consistent with the experimental results shown in Section 4-3.

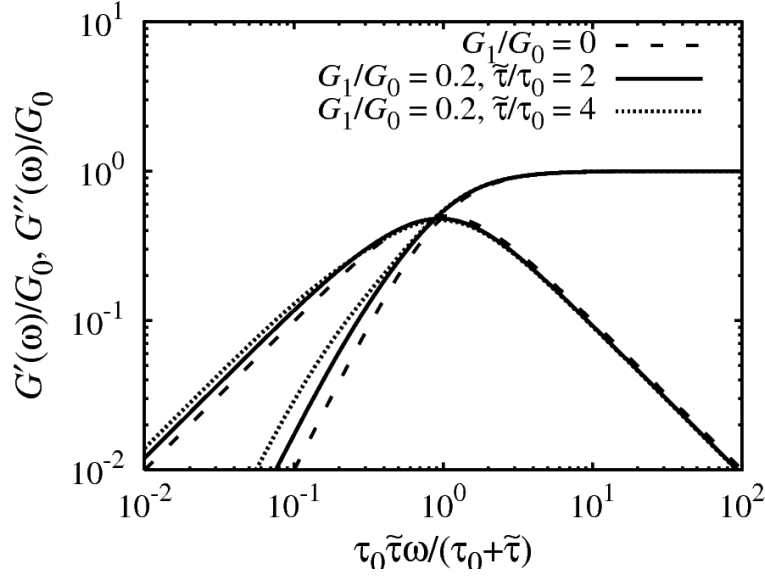


Figure 4-9: Rescaled storage and loss moduli calculated from the dense network model with some approximations. For simplicity, two characteristic relaxation times are assumed to be the same, $\tilde{\tau} = \tilde{\tau}(0) = \tilde{\tau}(1)$. The moduli are normalized by the characteristic modulus G_0 , and the angular frequency is normalized by the inverse relaxation time $[\tau_0 + \tilde{\tau}]/\tau_0\tilde{\tau}$.

Here, it would be fair to mention that Koga and Tanaka¹² also predicted the deviation of the storage and loss moduli from the single Maxwellian form. They attributed the deviation to the non-affine motion of micellar cores. However, their model predicts the narrowing of the storage and loss moduli, which is not consistent with the experimental result. In contrast, the dense network model shown in Section 4-3-2 predicts the broadening, which is in accord to the experiments.

4-5-2. Characteristic Modulus and Relaxation Time

Conventional transient network type models predict naive scaling of the relaxation time τ and characteristic modulus G_0 with the concentration c , $\tau \propto c^0$ and $G_0 \propto c^1$. This prediction is significantly different from experiments, implying that some essential factors are missing in the conventional models. In contrast, the dense and sparse network models may be able to explain the

experiments.

In the dense network model, the relaxation time can be estimated as $\tau \approx \tau_0 \tilde{\tau}(1) / [\tau_0 + \tilde{\tau}(1)]$.

This relaxation time explicitly depends on the relaxation time of micellar cores. Because the structure and dynamics of micellar cores strongly depends on the concentration of micelles, the relaxation time depends on the polymer concentration. In the sparse network model, the relaxation time becomes $\tau \approx m\tau_0$, and the number of bridges in a superbridge, m , depends on the concentration. Thus the relaxation time again depends on the polymer concentration. The origins of the concentration dependence of the dense and sparse network models are different, and therefore the concentration dependence is considered to change at a certain crossover concentration c_c .

The characteristic modulus of the dense network model coincides with its parameter, G_0 (G_1 does not contribute to the characteristic modulus). G_0 depends on the concentration through the number density of micellar cores and the bridge fraction. The sparse network model shows a similar but not identical concentration dependence. Thus the characteristic modulus also shows rather strong concentration dependence that changes at the crossover concentration c_c .

4-6. Conclusion

The concentration dependence of linear rheological properties of HEUR solutions is examined in this chapter. It was shown that the storage and loss moduli of HEUR solutions consist of two different modes; the fast and slow modes. These modes show different temperature dependence. The fast mode corresponds to the local relaxation of HEUR chains whereas the slow mode, to the

reassociation of chain ends. The frequency dependence of the storage and loss moduli depends on the concentration.

To reproduce experimental data, new transient network type models have been developed. By considering the sparseness of the network, two transient network type models (the sparse and dense network models) were formulated. In these models, the spatial distribution of the micellar cores is explicitly coupled with the reassociation dynamics. The micellar distribution and bridge fraction depend on the concentration, and these models can reproduce, at least qualitatively, the concentration dependence of linear rheological properties observed in experiments. The concentration dependence of nonlinear rheological properties deduced from those models is examined in Chapter 5.

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Chapter 5: Concentration Dependence of Nonlinear Viscoelasticity of HEUR Aqueous Solutions

5-1. Introduction

In Chapter 4, the concentration (c) dependence of the linear viscoelasticity of the HEUR aqueous solutions was examined. The experimental results showed that the c dependence changes at the crossover concentration $c_c \approx 4\text{wt}\%$. Below this crossover concentration, the storage and loss moduli were well expressed by the single Maxwellian form. The relaxation time τ and the characteristic modulus G_0 were found to depend on c rather strongly. In contrast, at larger $c > c_c$, the storage and loss moduli deviated from the single Maxwellian form and the c dependence of τ and G_0 became considerably weaker. These experimental observations would reflect structural change from the sparse network (at low c) to the dense network (at large c), the former mainly consisting of superbridges whereas the latter, of single-chain bridges.

The nonlinear viscoelastic properties should also change with c strongly, given that the network structure changes with c as discussed for linear properties in Chapter 4. Chapter 3 examined the nonlinear properties of the 1wt% HEUR aqueous solution, and that solution was in the sparse network regime (as judged from Figure 4-6). As the concentration is increased, the rheological properties of the HEUR solution may ultimately approach those of triblock copolymer melts. Triblock copolymer melts do not exhibit the shear thickening of the viscosity, which suggests lack of thinning also for the HEUR solutions at high c . Thus, it is worth examining the c dependence of the nonlinear viscoelasticity of HEUR aqueous solutions.

In this chapter, at first, the sparse and dense network models developed in Chapter 4 are applied to the HEUR aqueous solutions under steady shear. It will be demonstrated that the sparse and dense networks show different shear rate dependence, and that the sparse network model reduces to the anisotropic bridge formation model proposed in Chapter 3. Then the concentration dependence of the magnitudes of shear thickening and thinning of the HEUR solutions is systematically examined. Comparison of the theoretical predictions with the experimental data confirms that the shear thickening is indeed due to the anisotropy of the superbridge formation dynamics in the sparse network.

5-2. Theoretical Model

5-2-1. Shear Viscosity and First Normal Stress Coefficient

As shown in Chapter 4, the concentration dependence of the linear viscoelasticity of aqueous solutions of HEUR (having hexadecyl groups at the chain ends) can be reasonably explained by the transient network type models for sparse and dense networks. In this section, the same models are utilized to calculate nonlinear viscoelasticity.

To analyze the shear thickening and thinning, the steady state under the shear should be considered. As explained in Chapter 4, it would be reasonable to firstly consider the dense network model. From the expression of the stress tensor, eq (4-24), the shear viscosity $\eta(\dot{\gamma})$ and the first normal stress coefficient $\Psi_1(\dot{\gamma})$ under the steady shear are formulated as

$$\eta(\dot{\gamma}) = \frac{n_0 \rho_0 k_B T}{2\dot{\gamma}} \int d\mathbf{r} \frac{\partial u(\mathbf{r})}{\partial r_x} \frac{\partial u(\mathbf{r})}{\partial r_y} P_{ss}(\mathbf{1}, \mathbf{r}) \quad (5-1)$$

$$\Psi_1(\dot{\gamma}) = \frac{n_0 \rho_0 k_B T}{2\dot{\gamma}^2} \int d\mathbf{r} \left[\frac{\partial u(\mathbf{r})}{\partial r_x} r_x - \frac{\partial u(\mathbf{r})}{\partial r_y} r_y \right] P_{ss}(\mathbf{r}) \quad (5-2)$$

where $\dot{\gamma}$ is the shear rate. The steady state bridge distribution function, $P_{ss}(\mathbf{r})$, depends on the steady state micellar core distribution function $\Phi_{ss}(\mathbf{r})$, whereas $\Phi_{ss}(\mathbf{r})$ is specified as

$$L_{FP,ss}(0)\Phi_{ss}(\mathbf{r}) = 0 \quad (5-3)$$

Here, $L_{FP,ss}$ is the Fokker-Planck operator under the steady shear at the rate $\dot{\gamma}$.

The calculation of the explicit form of $\Phi_{ss}(\mathbf{r})$ is practically intractable, and some approximations and/or simplifications are required, as was the case also for the calculation of the relaxation modulus in Chapter 4. Nevertheless, fortunately, some properties of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ can be deduced even without the explicit form of $\Phi_{ss}(\mathbf{r})$. The loop and bridge distribution functions in the steady state are given by

$$P_{ss}(0) = \left[1 + \xi \int d\mathbf{r} e^{-3\mathbf{r}^2/2R_0^2} \Phi_{ss}(\mathbf{r}) \right]^{-1} \quad (5-4)$$

$$P_{ss}(\mathbf{r}) = P_{ss}(0) \xi \sum_k \tau_0^k L_{FP,ss}^k(1) e^{-3\mathbf{r}^2/2R_0^2} \Phi_{ss}(\mathbf{r}) \quad (5-5)$$

Thus, eqs (5-1) and (5-2) can be rewritten as

$$\eta(\dot{\gamma}) = \frac{n_0 \rho_0 \xi k_B T}{2\dot{\gamma}} P_{ss}(0) \int d\mathbf{r} \frac{3r_x r_y}{R_0^2} \sum_k \tau_0^k L_{FP,ss}^k(1) e^{-3\mathbf{r}^2/2R_0^2} \Phi_{ss}(\mathbf{r}) \quad (5-6)$$

$$\Psi_1(\dot{\gamma}) = \frac{n_0 \rho_0 \xi k_B T}{2\dot{\gamma}^2} P_{ss}(0) \int d\mathbf{r} \frac{3(r_x^2 - r_y^2)}{R_0^2} \sum_k \tau_0^k L_{FP,ss}^k(1) e^{-3\mathbf{r}^2/2R_0^2} \Phi_{ss}(\mathbf{r}) \quad (5-7)$$

These expressions explicitly depend on the steady state micellar core distribution, $\Phi_{ss}(\mathbf{r})$, which implies that the anisotropy of the micellar core distribution under steady shear affects $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$. Namely, the shear rate dependence of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ can change with this anisotropy.

For the sparse network model, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ can be obtained as

$$\bar{P}_{ss}(0) = \left[1 + \bar{\xi} \int d\mathbf{r} e^{-3\mathbf{r}^2/2R_0^2} \tilde{\Phi}_{ss}^{[m]}(\mathbf{r}) \right]^{-1} \quad (5-8)$$

$$\eta(\dot{\gamma}) = \frac{\bar{n}_{eff} \rho_0 \bar{\xi} k_B T}{\dot{\gamma}} \bar{P}_{ss}(0) \int d\mathbf{r} \frac{3}{mR_0^2} \left[r_x r_y + \left(\frac{\tau_0 \dot{\gamma}}{m} \right) r_x^2 \right] e^{-3\mathbf{r}^2/2mR_0^2} \tilde{\Phi}_{ss}^{[m]}(\mathbf{r}) \quad (5-9)$$

$$\begin{aligned} \Psi_1(\dot{\gamma}) = & \frac{\bar{n}_{eff} \rho_0 \bar{\xi} k_B T}{\dot{\gamma}^2} \bar{P}_{ss}(0) \int d\mathbf{r} \frac{3}{mR_0^2} \left[r_x^2 - r_y^2 + 2 \left(\frac{\tau_0 \dot{\gamma}}{m} \right) r_x r_y + 2 \left(\frac{\tau_0 \dot{\gamma}}{m} \right)^2 r_y^2 \right] \\ & \times e^{-3\mathbf{r}^2/2mR_0^2} \tilde{\Phi}_{ss}^{[m]}(\mathbf{r}) \end{aligned} \quad (5-10)$$

As noted from eqs (5-9) and (5-10), $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ depend on the (weighed) convolution of the micellar core distribution function, and this convolution has a stronger anisotropy than $\Phi_{ss}(\mathbf{r})$ itself. Thus the nonlinear viscoelasticity of the sparse network model is expected to be much more complex than that of the dense network model. In other words, the anisotropy is enhanced and the shear thickening and thinning behavior become more pronounced as the concentration decreases.

5-2-2. Power-Series Expansion with Respect to Shear Rate

The expressions of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ explained in the previous subsection depend on $\Phi_{ss}(\mathbf{r})$, but a simple, explicit expression of $\Phi_{ss}(\mathbf{r})$ cannot be obtained. Thus, some additional approximations and/or simplifications are required for analysis of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$. If the shear rate is not large, it would be reasonable to expand the distribution functions with respect to $\dot{\gamma}$ around the equilibrium distribution functions. The following arguments are limited for the sparse network exhibiting strong anisotropy. Because the equilibrium bond distribution function is Gaussian, the function $\tilde{\Phi}_{ss}^{[m]}(\mathbf{r})$ is naturally expanded with the Hermite polynomials being utilized as the expansion base.

$$\begin{aligned}\tilde{\Phi}_{ss}^{[lm]}(\mathbf{r}) = & \left(\frac{3}{2\pi m R_0^2} \right)^{3/2} \sum_{i,j,k} B_{i,j,k}(\dot{\gamma}) 2^{-(i+j+k)/2} \\ & \times H_i \left(\frac{\sqrt{3}r_x}{\sqrt{2m}R_0} \right) H_j \left(\frac{\sqrt{3}r_y}{\sqrt{2m}R_0} \right) H_k \left(\frac{\sqrt{3}r_z}{\sqrt{2m}R_0} \right)\end{aligned}\quad (5-11)$$

Here, $B_{i,j,k}(\dot{\gamma})$ is the $\dot{\gamma}$ -dependent expansion coefficient. The shear viscosity and the first normal stress coefficient can be expressed in terms of $B_{i,j,k}(\dot{\gamma})$, just in the same way as in Chapter 3.

$$\eta(\dot{\gamma}) = \frac{\bar{n}_{eff} \rho_0 \bar{\xi} k_B T}{\dot{\gamma} [1 + \bar{\xi} B_{0,0,0}(\dot{\gamma})]} \left[B_{1,1,0}(\dot{\gamma}) + \left(\frac{\tau_0 \dot{\gamma}}{m} \right) [B_{0,0,0}(\dot{\gamma}) + 2B_{0,2,0}(\dot{\gamma})] \right] \quad (5-12)$$

$$\begin{aligned}\Psi_1(\dot{\gamma}) = & \frac{\bar{n}_{eff} \rho_0 \bar{\xi} k_B T}{\dot{\gamma}^2 [1 + \bar{\xi} B_{0,0,0}(\dot{\gamma})]} \left[B_{2,0,0}(\dot{\gamma}) - B_{0,2,0}(\dot{\gamma}) + \left(\frac{\tau_0 \dot{\gamma}}{m} \right) B_{1,1,0}(\dot{\gamma}) \right. \\ & \left. + \left(\frac{\tau_0 \dot{\gamma}}{m} \right)^2 [B_{0,0,0}(\dot{\gamma}) + 2B_{0,2,0}(\dot{\gamma})] \right]\end{aligned}\quad (5-13)$$

The $\dot{\gamma}$ dependence of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ is determined by the dependence of $B_{0,0,0}$, $B_{1,1,0}$, $B_{2,0,0}$, and $B_{0,2,0}$. $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ depend on different expansion coefficients, and thus they exhibit different types of nonlinearity (as discussed in Chapter 3).

Because the expansion coefficients $B_{i,j,k}$ depend on the steady state micellar core distribution $\Phi_{ss}(\mathbf{r})$, they depend on the concentration rather strongly. Moreover, the anisotropy of the micellar core distribution becomes larger as the functionality of the network decreases. Thus the shear rate dependence can be relatively complex at low c . Namely, the shear thickening behavior is expected to clearly emerge only at low c in the sparse network regime, given that the thickening reflects the anisotropy of the reassociation dynamics. Consequently, the shear thickening and thinning behavior would change with c , and the shear rate dependence of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ would become relatively simple at high c .

5-3. Experimental

To validate the expectation explained in Section 5-2, the concentration dependence of the nonlinear viscoelasticity was examined for aqueous solutions of HEUR having hexadecyl groups at the chain ends (cf. Table 2-1). The HEUR concentration was varied in a range of $c = 1$ -10 wt %. (These solutions were identical to those examined in Chapter 4.) The nonlinear viscoelasticity measurements were performed with the same instrument and fixture as in Chapter 4 (MCR-301 rheometer (Anton Paar), and a cone-plate type fixture with the diameter $d = 75\text{mm}$ and the cone angle $\theta = 1^\circ$). The steady-state values of the shear stress and the first normal stress difference were measured at 25°C .

For the 1wt% HEUR aqueous solution, the velocity field was also determined by the particle imaging velocimetry. Hollow silica particles (HGS-10, Dantec Dynamics) with the diameter $10\mu\text{m}$ were utilized as tracer particles for the imaging. The tracer particles were dispersed in the 1wt% HEUR aqueous solution at the particle concentration of 800 ppm (w/w). Such dilute particles did not disturb the rheological properties. The nonlinear properties of this 1wt% HEUR solution containing the particles were measured with an ARES rheometer (TA Instruments) with a cone-plate fixture with the diameter $d = 50\text{mm}$ and the cone angle $\theta = 2.3^\circ$. During the measurements, the particle position was also recorded by a high-speed video camera (VW-6000, Keyence) from the edge of the fixture. The time-evolution of the particle position near the sample edge can be detected by this procedure, and differentiation of the position of the particles gave the velocity profiles of the sample (near the edge).

5-4. Results and Discussions

5-4-1. Concentration Dependence of Shear Viscosity and First Normal Stress Coefficient

For the HEUR *aq* solutions with $c = 1 - 10$ wt%, Figures 5-1 and 5-2 show the steady state viscosity $\eta(\dot{\gamma})$ and first normal stress coefficient $\Psi_1(\dot{\gamma})$. The horizontal lines indicate that the zero-shear viscosity, $\eta_0(=[G''/\omega]_{\omega \rightarrow 0})$ and zero-shear first normal stress coefficient $\Psi_{1,0} = 2J_e\eta_0^2$ ($=2[G'/\omega^2]_{\omega \rightarrow 0}$) evaluated from the linear viscoelastic storage and loss moduli measured in Chapter 4. ($J_e = [G'/G'']_{\omega \rightarrow 0}$ is the steady state recoverable compliance.)

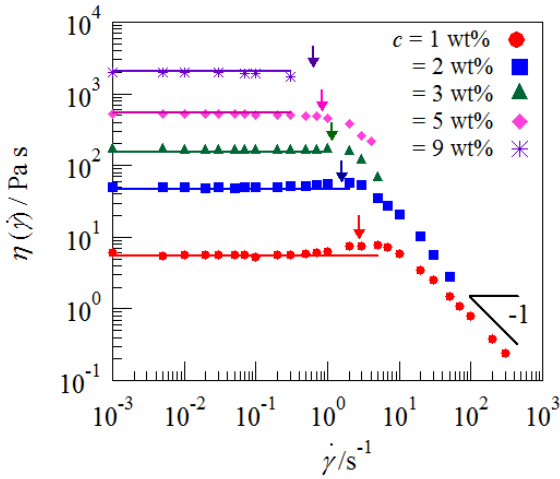


Figure 5-1. Steady state viscosity of the HEUR *aq* solutions at $T = 25^\circ\text{C}$. Horizontal lines represents zero-shear viscosity evaluated from the linear viscoelastic loss modulus, and the arrows, the relaxation frequency in the linear regime, $1/\tau$.

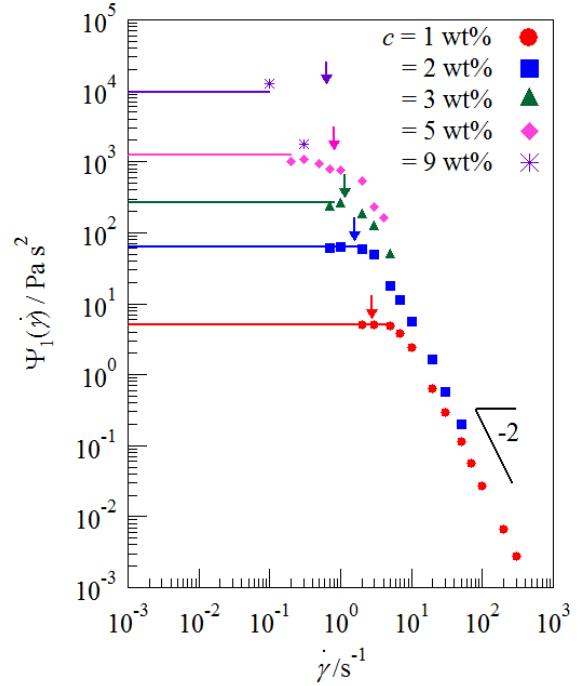


Figure 5-2. Steady state first normal stress coefficient data of the HEUR *aq* solutions at $T = 25^\circ\text{C}$. Horizontal lines represent the coefficient in the zero-shear regime evaluated from linear viscoelastic data. The arrows indicate the relaxation frequency in the linear regime, $1/\tau$.

For the HEUR solutions examined in Figures 5-1 and 5-2, the linear viscoelastic relaxation time τ and the characteristic modulus G_0 have been measured in Chapter 4. Both τ and G_0 change their

c dependence at $c_c \cong 4$ wt%; cf. Figure 4-6. This change was associated with a change of the linear relaxation mode distribution from single-Maxwellian ($c < c_c$) to broadened non-single Maxwellian ($c > c_c$) distribution. These changes of the linear behavior suggested a change in the HEUR network structure at equilibrium with increasing c beyond c_c (that is assigned as the change from the sparse network to dense network, as explained in Chapter 4).

The corresponding change is noted also for $\eta(\dot{\gamma})$ in the nonlinear regime; cf. Figure 5-1. The arrows therein indicate the linear relaxation frequency, $1/\tau$. For $c \leq 3$ wt% ($c < c_c$), the zero-shear behavior ($\eta(\dot{\gamma}) = \eta_0$) seen at the shear rates $\dot{\gamma} \ll 1/\tau$ is followed by thickening ($\eta(\dot{\gamma}) > \eta_0$) at $\dot{\gamma} \sim 1/\tau$ and further by thinning ($\eta(\dot{\gamma}) < \eta_0$) at $\dot{\gamma} \gg 1/\tau$. (For the 1 wt% solution, the flow was confirmed to be uniform in the zero-shear and thickening regimes but become non-uniform in the thinning regime, as shown later in Figure 5-4.) In contrast, for $c > c_c$, the thickening behavior vanishes and $\eta(\dot{\gamma})$ exhibits a direct crossover from the zero-shear behavior to the thinning behavior on the increase of $\dot{\gamma}$ above $1/\tau$. This result is in harmony with the disappearance of the thickening with increasing c found by Ma and Cooper¹ (although they did not report the first normal stress coefficient data).

This change of $\eta(\dot{\gamma})$ can be most clearly demonstrated in Figure 5-3 where the maximum $\eta(\dot{\gamma})$ values of respective solutions in the entire range of $\dot{\gamma}$ examined are normalized by the η_0 values and plotted against c . The $\eta_{\max}/\eta_0$ ratio gradually approaches unity with increasing c and this approach completes at $c_c \approx 4$ wt%, suggesting that the change of the network structure (from the sparse network to the dense network) essentially completes at c_c .

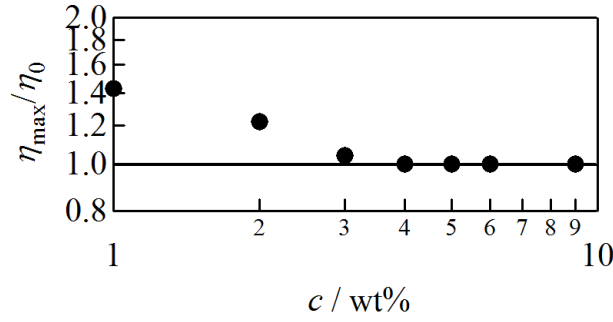


Figure 5-3. Concentration dependence of the magnitude of shear thickening of η at 25°C.

In relation to the behavior of $\eta(\dot{\gamma})$ explained above, it should be noted that the first normal stress coefficient $\Psi_1(\dot{\gamma})$ never exhibits the thickening, even at $\dot{\gamma} \sim 1/\tau$ where the thickening of $\eta(\dot{\gamma})$ is observed for $c < c_c$, as discussed in Chapter 3 and also demonstrated in Figures 5-1 and 5-2. This fact was the key in the discussion in Chapter 3 that the nonlinear flow behavior of the HEUR solutions cannot be consistently explained by conventional models considering the finite extensible nonlinear elasticity (FENE) and flow-induced increase of the strand number density. (The conventional models predict that $\Psi_1(\dot{\gamma})$ mostly exhibits the thickening together with $\eta(\dot{\gamma})$.) Furthermore, on the basis of that discussion, the “sparse network” and “dense network” models were developed in Chapter 4 and their nonlinearities in the steady state were characterized in the earlier subsection of this chapter. One of the main consequence of the model prediction, the crossover from the sparse network to dense network regime for both linear and nonlinear behavior is clearly confirmed in Figures 5-1, 5-2, and 5-3. Namely, the thickening of $\eta(\dot{\gamma})$ associated with no nonlinearity of $\Psi_1(\dot{\gamma})$ was observed only at low $c < c_c$ where the single-Maxwellian behavior prevails in the linear regime (cf. Figure 4), as deduced from those models. The simpler nonlinearity deduced from the dense network model, *i.e.*, direct crossover from the linear regime to the thinning

regime with increasing $\dot{\gamma}$ for both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$, is also consistent with the experimental observation. Thus, the nonlinear data of the HEUR solutions at various c also lend support to the “sparse network” and “dense network” models, which in turn suggests the importance of the network strand structure (superbridge at low c and single-chain bridge at high c) on the nonlinear properties.

5-4-2. Velocity Field in 1wt% HEUR Aqueous Solution

Berret et al.² and Sprakel et al.³ reported the flow non-uniformity (shear banding) of HEUR solutions in the thinning regime. This non-uniformity could change the nonlinear rheological behavior of the solutions. Thus, for the 1 wt% HEUR solution exhibiting both thickening and thinning of $\eta(\dot{\gamma})$ (in the sparse network regime), the local flow velocity profile was examined via particle-tracking velocimetry in a cone-and-plate geometry. Under steady rotation of the plate (against the fixed cone), the silica particles near the cone-plate edge were traced to evaluate their velocity v in the shear direction, as explained in Experimental section. The results are shown in Figure 5-4 as the plots of v against the height h of the particle from the cone surface normalized by the cone-and-plate gap H .

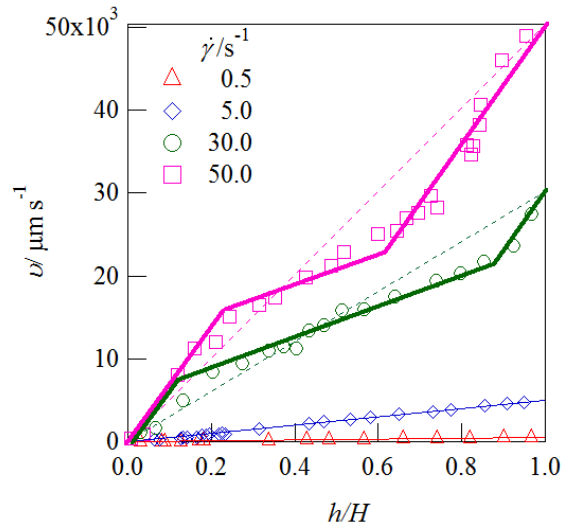


Figure 5-4. Flow velocity profiles determined for 1.0 wt% HEUR *aq* solution at 25°C. The solution contained 800 ppm hollow silica particles as the tracer. The applied (macroscopic-average) shear rate $\dot{\gamma}/\text{s}^{-1}$ is 0.5 (linear regime), 5.0 (thickening regime for η), and 30 and 50 (shear thinning regime).

As noted in Figure 5-4, the local velocity v varies linearly with the normalized height h/H in the entire range from $h/H = 0$ (cone) to $h/H = 1$ (plate) under the flow at macroscopic nominal shear rates of 0.5 s^{-1} (in the linear/zero-shear regime) and of 5.0 s^{-1} (in the thickening regime for η). For those cases, the flow was uniform and the real shear rate $\dot{\gamma}$ was constant/constant in the cone-and-plate gap, which allows the argument for the thickening in dilute solutions (sparse network) in the previous section to remain without change.

In contrast, under the flow at the nominal shear rate of 30 and 50 s^{-1} (in the thinning regime), v does not vary with h/H linearly but exhibits kinks. Thus, in the thinning regime, the real shear rate was not uniform in the cone-plate gap and shear bands were formed, as reported by Berret et al.² and Sprakel et al.³ This non-uniformity of the flow was not incorporated in the argument for the thinning in the previous section and the corresponding sparse network model. Nevertheless, the

essential part in the argument, thinning due to flow-induced disruption of the network, remains unchanged. The argument/model is to be refined just for a difference of the magnitude of the flow-induced dissociation in different shear bands. In the simplest scenario, this difference of the magnitude is determined by the lever rule, as discussed below.

Generally, shear bands are formed if a constitutive relation (between the steady shear stress and the shear rate) of a material has a non-monotonic form. Namely, if the constitutive relation gives the steady state shear stress $\sigma(\dot{\gamma})$ that firstly increases with $\dot{\gamma}$ on an increase of $\dot{\gamma}$ up to a lower critical rate $\dot{\gamma}_{c1}$ and then decreases with increasing $\dot{\gamma}$ and finally increases again with $\dot{\gamma}$, the uniform flow becomes unstable in a range of $\dot{\gamma}$ between $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$; cf. Figure 5-5. Here, $\dot{\gamma}_{c2}$ ($> \dot{\gamma}_{c1}$) is a higher critical rate defined by a relationship, $\sigma(\dot{\gamma}_{c2}) = \sigma(\dot{\gamma}_{c1})$.

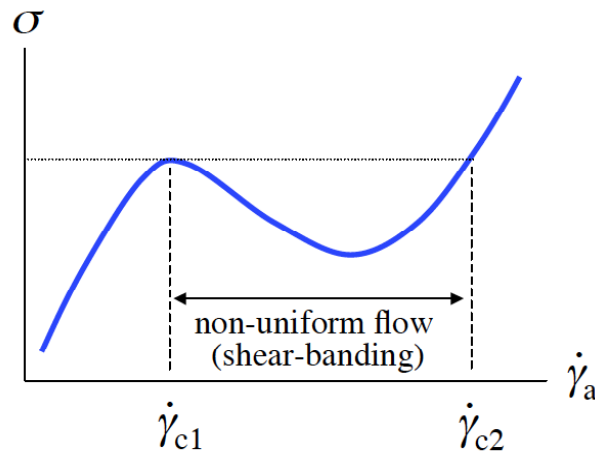


Figure 5-5. Schematic illustration of constitutive relation for shear banding.

For the above constitutive relation, the slow and fast shear bands flowing at the rates $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$ are formed for the macroscopic, nominal rate $\dot{\gamma}_a$ between $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$, and the fraction of the slow band ϕ_{c1} is determined by the lever rule³⁻⁵:

$$\dot{\gamma}_a = \phi_{c1} \dot{\gamma}_{c1} + (1 - \phi_{c1}) \dot{\gamma}_{c2} \quad (5-14)$$

Correspondingly, the macroscopically observed stress remains constant ($= \sigma(\dot{\gamma}_{c2}) = \sigma(\dot{\gamma}_{c1})$) for $\dot{\gamma}_a$ between $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$. Validity of the lever rule has been rather well established for various softmatters⁴ (including wormlike micelles of surfactants^{5,6}), although the underlying constitutive relation is subjected to controversial discussion in particular when the material is a solution and the different bands can have different concentrations.

For the 1 wt% HEUR solution in the thinning regime, the $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ data steeply decrease with the shear rate and are well described by empirical equations, $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-0.97}$ and $\Psi_1(\dot{\gamma}) \propto \dot{\gamma}^{-1.98}$ (cf. eq (3-5)). Thus, the shear stress σ ($= \eta\dot{\gamma}$) and the first normal stress difference N_1 ($= \Psi_1\dot{\gamma}^2$) is quite insensitive to the macroscopic, nominal shear rate $\dot{\gamma}_a$, which well corresponds to the stress plateau characteristic to the shear banding. From this point of view, the shear-banded flow velocity profile (Figure 5-4) was analyzed on the basis of eq (5-14) to estimate the critical shear rates, $\dot{\gamma}_{c1} \cong 18 \text{ s}^{-1}$ and $\dot{\gamma}_{c2} \cong 70 \text{ s}^{-1}$ commonly for $\dot{\gamma}_a = 30$ and 50 s^{-1} . The thick solid lines in Figure 5-4 shows the corresponding flow velocity profile: The fast bands flowing at $\dot{\gamma}_{c2}$ is formed near the cone and plate surfaces ($h/H \cong 0$ and 1), and the slow band flowing at $\dot{\gamma}_{c1}$ emerges between these fast bands.

Here, some comments need to be added for the above results. The recent theory by Sato, Yuan, and Kawakatsu⁷ suggests that the shear banding is similar to the thermodynamic first-order phase transition and just two bands (one fast band and one slow band) are formed in the most stable state under flow. Nevertheless, the 1 wt% HEUR solution formed three bands, two fast bands and one slow band (cf. Figure 5-4). Thus, the shear-banded structure in this solution would be a

meta-stable structure. The three bands could converge into two after a sufficiently long time. However, this convergence could be very slow and not achieved in the experimental time scale (because the system should overcome large energy barriers to realize the most stable state, as usual for macroscopic transition).

In addition, it should be noted that the lower critical rate for shear banding evaluated from the flow velocity profile, $\dot{\gamma}_{c1} \cong 18 \text{ s}^{-1}$, is close to a characteristic shear rate for the onset of validity of the empirical equations $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-0.97}$ and $\Psi_1(\dot{\gamma}) \propto \dot{\gamma}^{-1.98}$ (cf. eq (3-5)), that is, the onset of $\dot{\gamma}_a$ -insensitive plateau of σ and N_1 . This result is consistent with the simplest scenario of shear banding explained above. However, the data (Figures 5-1 and 5-2) show a puzzling feature that the empirical equations are valid and σ and N_1 stay in the plateau zone up to the highest rate examined, $\dot{\gamma}_{a,\max} = 300 \text{ s}^{-1}$, whereas the upper critical rate of shear banding evaluated from the velocity profile, $\dot{\gamma}_{c2} \cong 70 \text{ s}^{-1}$, is considerably lower than this $\dot{\gamma}_{a,\max}$. This result is contradicting to the simplest scenario giving the increase of σ and N_1 on an increase of $\dot{\gamma}_a$ above $\dot{\gamma}_{c2}$. Thus, the shear banding in the 1 wt% HEUR solution is not that simple, and there should be some mechanisms not considered in the simplest scenario. For example, different bands might have different HEUR concentrations to violate the simplest scenario. Fluid fracture reported by Berret and S  r  ro² could also violate the simplest scenario and result in nontrivial behavior of σ and N_1 . Slips at the interface and/or between bands could give a similar effect as well. This puzzling problem demonstrates rich physics in the thinning/shear-banding phenomena.

5-5. Conclusion

This chapter has devoted for test of nonlinear flow behavior of HEUR *aq* solutions having various concentrations c . The thickening of the steady state viscosity η became less significant with increasing c and was not detectable at $c \geq c_c$ E 4 wt%. This change of the nonlinear feature well corresponded to changes of the c dependence of the linear viscoelastic relaxation time τ and the characteristic modulus G_0 seen at c_c , suggesting a difference of the associated HEUR network structure at $c < c_c$ and $c > c_c$. Specifically, at $c < c_c$, the sparse network having superbridges as its stands appears to have been formed. Multiplicity of the dissociation sites (micellar cores) in those superbridge strands and the corresponding reassociation probability being sensitive to anisotropy of the distribution of those cores possibly resulted in the observed thickening of η associated with linear ($\dot{\gamma}$ -insensitive) first normal stress coefficient Ψ_1 as well as the single-Maxwellian linear viscoelastic relaxation with strongly c -dependent τ and G_0 , as suggested from the sparse transient network model developed in Chapter 4.

In contrast, at $c > c_c$, the dense network having individual HEUR chains as its stands would have been formed. The effect of multiplicity mentioned above should vanish for reassociation of those HEUR chains thereby possibly erasing the thickening feature of η and resulting in the broadened non-Maxwellian relaxation associated with rather weakly c -dependent τ and G_0 observed for concentrated solutions, as suggested from the dense transient network model. Thus, the sparse and dense transient network models capture the changes of the nonlinear and linear rheological features of the HEUR solutions with c qualitatively but consistently, which in turn suggests the

importance of the strand structure for those features.

For the 1 wt% HEUR solution (in the sparse network regime), the local flow velocity profile was also examined with the particle-tracking velocimetry. At low and intermediate macroscopic, nominal shear rates $\dot{\gamma}_a = 0.5 \text{ s}^{-1}$ (in the linear/zero-shear regime) and $\dot{\gamma}_a = 5.0 \text{ s}^{-1}$ (in the thickening regime for η), the flow was found to be uniform and thus the local $\dot{\gamma}$ agreed with the macroscopic $\dot{\gamma}_a$ throughout the cone-and-plate gap. (Consequently, the above argument for the thickening is valid under the observed flow profile.) In contrast, at higher $\dot{\gamma}_a$ where both η and Ψ_1 exhibited thinning, the flow was not uniform and two fast shear bands and one slow band were observed. Thus, the thinning of η and Ψ_1 was actually reflecting the flow-induced disruption of the HEUR network occurring to a different extent in different bands, which is consistent with the simplest scenario of shear banding. Nevertheless, the shear stress σ and the first normal stress difference N_1 of the 1 wt% HEUR solution remained constant even at high $\dot{\gamma}_a$ exceeding the shear rate $\dot{\gamma}_{c2}$ in the fast band, which was contradicting to the simplest scenario giving the increase of σ and N_1 at $\dot{\gamma}_a > \dot{\gamma}_{c2}$. This result could be related to several factors not considered in that scenario, such as the concentration difference in different bands. This puzzling feature in turn demonstrates rich physics in the thinning/shear-banding phenomena.

Appendix 5-A. Derivation of Anisotropic Bridge Formation Model from Sparse Network Model

The anisotropic bridge formation model proposed in Chapter 3 can be derived from the sparse network model developed in Chapter 4 with some approximations. This derivation is explained in this Appendix.

For the sparse network model, some approximations can be reasonably introduced, as discussed in Chapter 4. Namely, the dissociation time scale is approximated to be constant (eq (4-25)), the bond potential is approximated to be harmonic (eq (4-26)), and the equilibrium Fokker-Planck operator can be neglected (eq (4-32)). Because the active bond distribution function plays a central role in the anisotropic bridge formation model, it would be reasonable to introduce the normalized active bond distribution function defined by

$$\psi(\mathbf{r}, t) = \frac{\bar{P}_{eq}(\mathbf{r}, t)}{1 - \bar{P}_{eq}(0)} \quad (5-A1)$$

The stress tensor is expressed in terms of this $\psi(\mathbf{r}, t)$

$$\boldsymbol{\sigma} = \nu_{eff} k_B T \int d\mathbf{r} \left[\frac{3\mathbf{r}\mathbf{r}}{r_0^2} - \mathbf{1} \right] \psi(\mathbf{r}) \quad (5-A2)$$

where r_0^2 is the mean-square average end-to-end distance, and $\nu_{eff} = \bar{n}_{eff} \rho_0 [1 - \bar{P}_{eq}(0)]$ is the effective number density of active bonds. Then, the dynamic equation (4-21) can be rewritten as

$$\frac{\partial \psi(\mathbf{r}, t)}{\partial t} = -\dot{\gamma} r_y \frac{\partial \psi(\mathbf{r}, t)}{\partial r_x} + \frac{1}{\bar{\tau}_0} \phi(\mathbf{r}, t) - \frac{1}{\bar{\tau}_0} \psi(\mathbf{r}, t) \quad (5-A3)$$

with $\bar{\tau}_0 = \tau_0 / m$ and

$$\phi(\mathbf{r}, t) = m \bar{\xi} e^{-3\mathbf{r}^2 / 2r_0^2} \tilde{\Phi}^{[lm]}(\mathbf{r}, t) \frac{\bar{P}_{eq}(0)}{1 - \bar{P}_{eq}(0)} \quad (5-A4)$$

Eq (5-A3) is formally identical to the time evolution equation for the anisotropic bridge formation

model, and thus the sparse network model (with some approximations) reduces to the anisotropic bridge formation model.

It should be noticed that the anisotropy of the bridge formation process was discussed in Chapter 3 without microscopic information. From eqs (5-A3) and (5-A4), the source function ϕ is related to the micellar core correlation function. This implies that the microscopic origin of the anisotropic bridge formation is the anisotropy of the sites for the bridge formation. This mechanism seems to be physical reasonable, because a newly formed active bond (superbridge) must connect two micellar cores.

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Chapter 6: Rheology of Aqueous Solution of Hydrophobically Modified Ethoxylated Urethane (HEUR) with Fluorescent Probes at Chain Ends: Thinning Mechanism

6-1. Introduction

Hydrophobically-modified ethoxylated urethane (HEUR) is a representative water-soluble telechelic polymer that form a transient network structure. At high HEUR concentration c , this transient network spreads throughout the whole solution to govern slow rheological responses of the HEUR *aq* solutions. For example, these solutions exhibit the single-Maxwellian relaxation in the linear viscoelastic regime, as first noted by Annable et al.^{1,2} This relaxation behavior reflects the thermal reorganization (dissociation/association) of the HEUR network, and the relaxation time corresponds to the lifetime of the HEUR core acting as the physical crosslink for the network. The relaxation time and the viscosity of the HEUR *aq* solutions change with temperature, concentration, and type of the end groups, as revealed in extensive studies³⁻⁶ and further analyzed in Chapter 4 in this thesis. Furthermore, optical experiments have been made for solutions of HEUR chains containing fluorescent pyrenyl (Py) groups, either chemically attached to the chain end⁷ or just dissolved in the solutions⁸⁻¹⁰, to detect the fluorescent emission from excimers formed by the Py groups associated in the hydrophobic cores. The fluorescent emission data can be utilized to estimate, for example, the fraction of dangling chain ends in the HEUR *aq* solutions⁸. Those data, if combined with some statistical models, may also give an estimate of the aggregation number^{7,8}.

Under fast shear flow, the HEUR *aq* solutions exhibit significant nonlinear behavior, thickening

and thinning of the steady state viscosity $\eta(\dot{\gamma})$ ^{1,5,7,9-11,13-18}, which again reflects the transient nature of the HEUR network. Specifically, the thickening, often observed at shear rates $\dot{\gamma}$ just above the equilibrium relaxation frequency $1/\tau$, has been conventionally attributed to the finite extensible nonlinear elasticity (FENE) of the HEUR strands under fast shear^{11,13-15,19,20}, and/or the shear-induced increase of the number density n of effective network strands¹⁶⁻¹⁸. However, for a 1 wt% model HEUR *aq* solution, the thickening of $\eta(\dot{\gamma})$ is accompanied with no nonlinearity of the normal stress coefficient $\Psi_1(\dot{\gamma})$ and thus the above conventional mechanisms of thickening are not very adequate for this model solution, as fully described in Chapter 3 of this thesis. On the basis of this experimental fact, a Gaussian transient network model was formulated in Chapter 3. This model focused on delicate anisotropy in the creation (association) of network strands to successfully show that preferential creation of new strands in the shear gradient direction could result in the thickening of $\eta(\dot{\gamma})$ associated with no nonlinearity of $\Psi_1(\dot{\gamma})$.

The model was refined/extended in Chapter 4 to consider differences in the HEUR network structure at low c (e.g., 1 wt%) and high c . The network at low c is sparse and mainly sustained by superbridges (connected sequences of HEUR chains). A “sparse network” model considering dissociation/association of superbridges, that includes the Gaussian transient network model as a special case, predicts the single-Maxwellian relaxation in the linear regime and the nonlinear hardening of $\eta(\dot{\gamma})$ under shear flow at $\dot{\gamma}$ just above $1/\tau$ to mimic the behavior of low- c HEUR solution. Multiplicity of the association of the HEUR chains in each superbridge is the key resulting in this prediction. Indeed, a “dense network” model considering single-chain bridges in

high-c HEUR solutions predicts non-single Maxwellian relaxation and suppressed thickening. The corresponding crossover, from the sparse network behavior to the dense network behavior, has been confirmed experimentally in Chapters 4 and 5.

Differing from the behavior explained above, the thinning of $\eta(\dot{\gamma})$ seen at $\dot{\gamma} \gg 1/\tau$ is accompanied by thinning of $\Psi_1(\dot{\gamma})$. This feature suggests that the thinning reflects the shear-induced disruption of the HEUR network (decrease of τ). This assignment of the thinning mechanism sounds reasonable, but direct structural observation of the strand disruption was missing in literature. An exception is a paper by Richey et al.⁷ who reported fluorescent behavior of the Pyrene-tagged HEUR chains under flow. Nevertheless, even in that paper, the $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ data were not well analyzed in relation to the fluorescent data.

Thus, this chapter is devoted for rheological and optical experiments for a model HEUR chain having butylpyrenyl (Bu-Py) groups at the ends to examine the structural origin of shear thinning. It turned out that the fluorescent emission intensity from the excimers of Py groups (in the micellar cores) decreases only slightly on an increase of $\dot{\gamma} \gg 6/\tau$ well in the thinning regime. This result suggested that the thinning of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ is mostly due to shear-induced disruption of the network connectivity through conversion of the super-bridges into super-loops, both having the same structure of the cores and thus exhibiting the same fluorescent behavior. Details of these results are presented below.

6-2. Experimental

HEUR having butylpyrenyl (Bu-Py) groups at the chain ends, synthesized and characterized in Chapter 2 (cf. Table 2-1), was utilized. The material subjected to the rheological measurements was a 3.0 wt% aqueous solution of the HEUR sample in distilled water. Prescribed masses of water and HEUR were stirred for 24 hours to prepare the solution.

For this solution, rheological and fluorescent measurements were conducted with a stress-control laboratory rheometer, MCR-301 (Anton Paar). Dynamic measurements in the linear viscoelastic regime were conducted with a cone-plate (CP) fixture made of SUS-304 stainless steel. The cone/plate diameter was $d = 75$ mm, and the cone angle, $\theta = 1.0^\circ$. The storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured as functions of the angular frequency ω at several temperatures between 5 and 25°C. Those data obeyed the time-temperature superposition at low ω where the HEUR network exhibited the terminal relaxation (through its thermal reorganization). The data were reduced at 5°C.

The viscosity and first normal stress coefficient in the steady state, $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$, were measured at 5°C as a function of the shear rate $\dot{\gamma}$. (The relaxation of the HEUR solution was too fast to allow accurate measurements of the transient, viscosity and normal stress growth functions.) The measurements were made with two sets of CP fixture, one with $d = 75$ mm and $\theta = 1.0^\circ$ (the fixture explained above), and the other with $d = 40$ mm and $\theta = 5.7^\circ$ made of quartz.

The latter set of CP was utilized to measure, simultaneously with $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$, the fluorescent emission intensity $I_E(\dot{\gamma})$ from the excimers of Py groups associated in the hydrophobic

cores of the HEUR micelles. Ultraviolet (UV) light of the wavelength $\lambda = 340$ nm (fluorescent excitation trigger), obtained from a UV lamp (Max-301; Asahi Spectra), was introduced to this quartz CP fixture, and the fluorescent emission spectra were measured in a range of $\lambda = 350$ nm-650 nm with a spectrometer (PAM-11; Hamamatsu Photonics). Some Py groups transiently dissociate from the core and are isolated in the aqueous phase. The fluorescent emission from these dissociated Py groups (referred to as monomers) was observed at $\lambda_{em} = 370$ -410 nm, and that from the Py excimer, at $\lambda = 410$ -650 nm. The intensities of the monomer and excimer emission, $I_M(\dot{\gamma})$ and $I_E(\dot{\gamma})$, were measured as peak intensities at $\lambda = 377$ nm and 487 nm, respectively, and their ratio, $I_E(\dot{\gamma})/I_M(\dot{\gamma})$, was utilized as a measure of the number of the Py groups in the HEUR cores. (A slight fluctuation of the UV lamp intensity was canceled in this ratio.)

6-3. RESULTS

6-3-1. Linear viscoelastic behavior.

For the 3.0 wt% aqueous solution of HEUR, the storage and loss moduli data, $G'(\omega)$ and $G''(\omega)$, measured at several temperatures (5-25°C) obeyed the time-temperature superposition (tTS) in the range of ω examined. Figure 6-1 shows the master curves of those data reduced at $T_r = 5^\circ\text{C}$. The solid curves indicate the result of fitting with the single-Maxwellian model:

$$G'(\omega) = G_0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}, \quad G''(\omega) = G_0 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (6-1)$$

Here, G_0 (= 310 Pa) and τ (= 0.022 s) are the characteristic modulus and relaxation time, respectively. The fit is excellently achieved at low ω , as noted for similar HEUR solutions and also

for the model low-*c* HEUR solutions examined in Chapters 3 and 4. Thus, the Py-tagged HEUR *aq* solution is classified as the low-*c* HEUR solution being described by the “sparse network” model discussed in Chapters 4 and 5. The local intra-strand relaxation gives a non-Maxwellian character to the solution at high ω and disturbs the time-temperature superposition, as explained in Chapter 4. This local relaxation is too fast to be clearly detected in the experimental window. Nevertheless, a small deviation from the single Maxwellian fitting seen in Figure 6-1 can be attributed to the local relaxation.

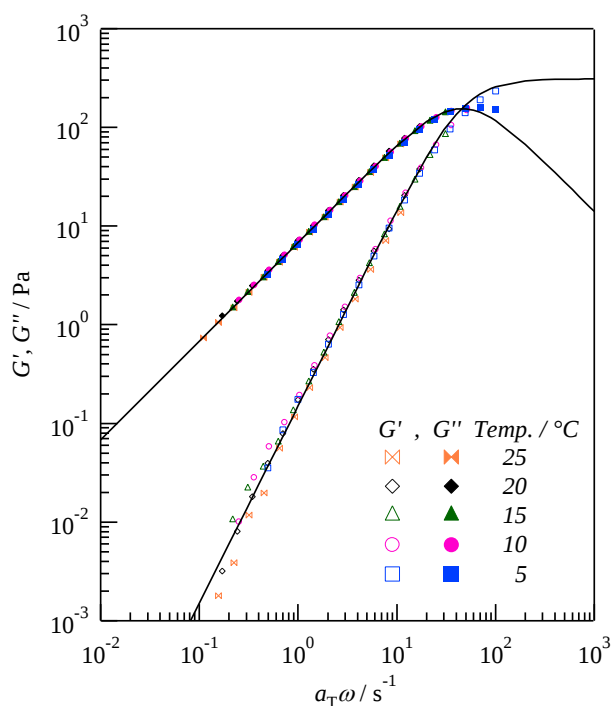


Figure 6-1. Master curves of storage and loss moduli of the 3.0 wt% HEUR *aq* solution reduced at 5°C. The solid curves indicate the results of fitting with single-Maxwellian form.

The single-Maxwellian terminal behavior of the HEUR solution is attributed to the thermal reorganization of the transient network occurring at the time τ . This reorganization occurs through dissociation/association of the Py groups at the HEUR chains, and the interior methylene

diphenyl-4,4'-diisocyanate groups (MDPDI; cf. Figure 1) are polar enough to exhibit no association, as suggested from the behavior of a similar HEUR chain having the interior MDPDI groups and end-capping hexadecyl groups. Consequently, the characteristic modulus G_0 prevailing at high ω (before the dissociation) is related to the entropy elasticity of the active strands, and the number density ν of those strands is estimated as

$$\nu = \frac{G_0}{k_B T} \cong 8.1 \times 10^{22} \text{ m}^{-3} \quad (6-2)$$

Here, k_B is the Boltzmann constant and T is the absolute temperature. This ν value is smaller than the number density of the HEUR chains, $\nu_0 = 2.9 \times 10^{23} \text{ m}^{-3}$ evaluated from the HEUR concentration and molecular weight, $c = 0.03 \text{ g cm}^{-3}$ and $M_n = 6.2 \times 10^4$.

The value of the ν/ν_0 ratio ($= 0.28$) suggests that the HEUR network in the solution is mainly sustained by superbridges and is regarded as the sparse network. This point can be further examined for the functionality f of the network (the average number of elastically active chains per micellar core). The functionality is roughly estimated to be $f \approx n\nu/\nu_0$ (where n is the association number⁸). For the 3 wt% HEUR solution examined in this chapter, the functionality is estimated as $f \approx 1.6$ (with $n \approx 6$ estimated by the fluorescent data in literature⁷), which is not large enough to form a dense network. This result lends support to the above assignment of the 3 wt% HEUR solution as the solution containing the sparse network that is mainly sustained by the superbridges.

Figure 6-2 shows the temperature dependence of the shift factor a_T for the master curves of G' and G'' . The Arrhenius behavior, $\ln a_T = E_a(T^{-1} - T_r^{-1})/R$ with R being the gas constant, is clearly noted, and the activation energy is evaluated to be $E_a \cong 76 \text{ kJ mol}^{-1}$. This E_a value can be assigned

as the association energy of the Bu-Py groups at the HEUR chain ends that stabilizes the HEUR network in our solution. From the energy competition argument based on the E_a value (as presented in Appendix of Chapter 3), the nonlinear elasticity (FENE) effect is expected to be negligible in the 3 wt% HEUR solution.

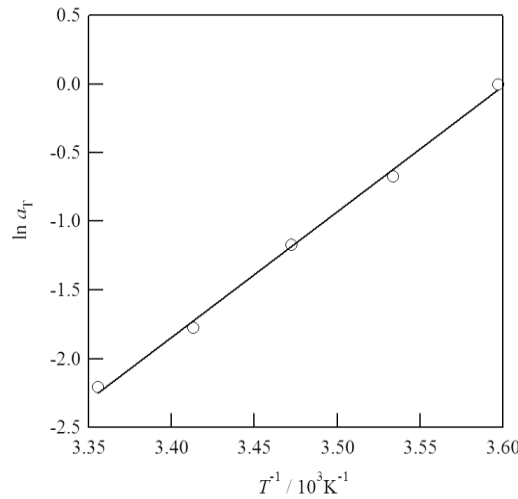


Figure 6-2. Temperature dependence of the shift factor for the master curves shown in Figure 6-1.

6-3-2. Nonlinear flow and fluorescent behavior.

Figure 6-3 shows the steady state viscosity $\eta(\dot{\gamma})$ and the first normal stress coefficient $\Psi_1(\dot{\gamma})$ measured for the 3.0 wt% HEUR solution at 5°C. The data obtained with the cone-plate (CP) fixtures with the diameter $d = 75$ mm and the cone angle $\theta = 1.0^\circ$ (large unfilled symbols) and with $d = 40$ mm and $\theta = 5.7^\circ$ (small filled symbols) agree with each other. The horizontal dashed lines indicate respective zero-shear values, $\eta_0 (= [G''/\omega]_{\omega \rightarrow 0})$ and $\Psi_{1,0} (= 2\eta_0^2 J_e = 2[G'/\omega^2]_{\omega \rightarrow 0})$, obtained from the linear viscoelastic G' and G'' data.

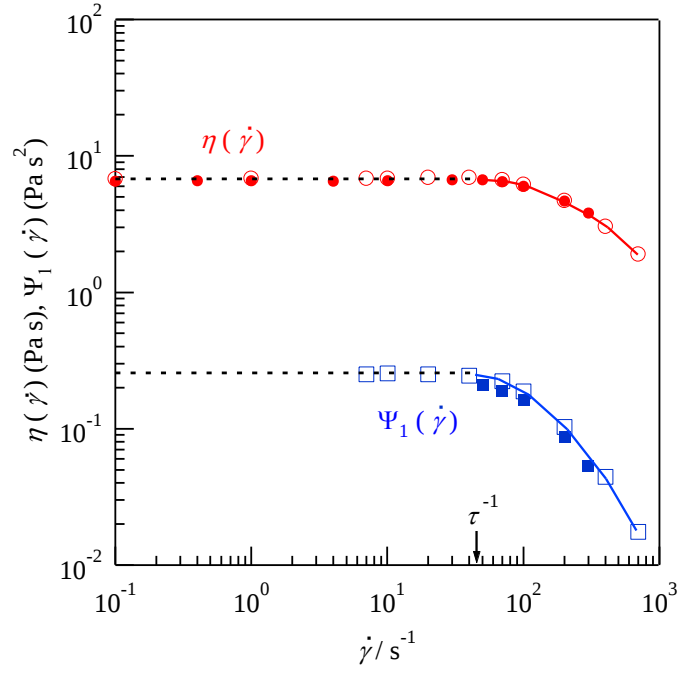


Figure 6-3. Steady state viscosity and first normal stress coefficient measured for the 3.0 wt% HEUR *aq* solution at 5°C. The horizontal dashed lines indicate the zero-shear values, η_0 and $\Psi_{1,0}$ ($=2\eta_0^2 J_e$), evaluated from the linear viscoelastic G' and G'' data.

The CP fixture with $d = 40$ mm and $\theta = 5.7^\circ$ (made of quartz) was utilized to measure, under flow (together with the rheological data), the intensity of the fluorescent emission from the pyrenyl (Py) groups at the HEUR chain ends. A typical example of the emission spectra is shown in Figure 6-4, where I_M shows the emission from the isolated Py group (monomer) transiently dissociating from the micellar core into the aqueous phase, and I_E , the emission from the excimer of the Py groups associated in the hydrophobic core. These $I_M(\dot{\gamma})$ and $I_E(\dot{\gamma})$ are quantified as the emission peak intensity at $\lambda = 377$ nm and 487 nm, respectively, and the spectra shown in Figure 6-4 have been normalized by $I_M(\dot{\gamma})$ (at $\lambda = 377$ nm) so as to cancel a slight fluctuation of the excitation UV intensity. A ratio, $I_E(\dot{\gamma})/I_M(\dot{\gamma})$, is utilized as a measure of the number of the Py groups associated in the HEUR cores. Figure 6-5 shows changes of the $I_E(\dot{\gamma})/I_M(\dot{\gamma})$ ratio with the shear rate $\dot{\gamma}$.

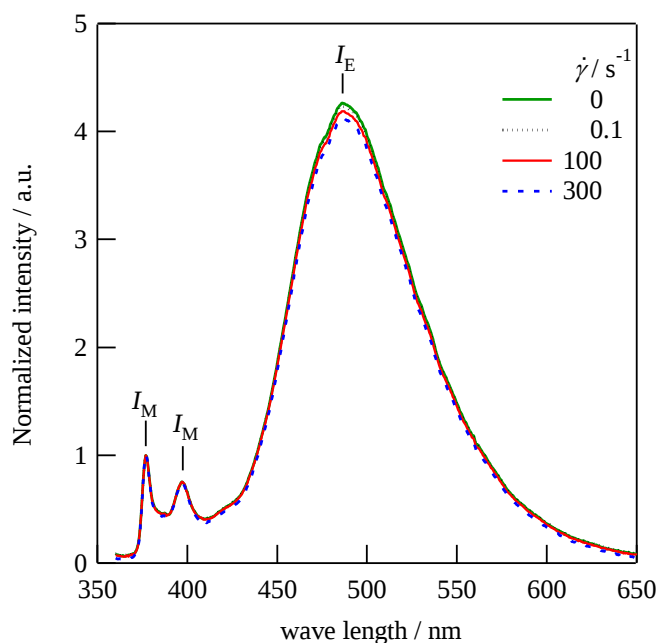


Figure 6-4. Intensity of fluorescent emission from the 3.0 wt% HEUR *aq* solution in the quiescent state ($\dot{\gamma} = 0$) and under steady shear flow at 5 °C. I_M and I_E indicate the emission from the pyrenyl group (attached at the chain ends) in the isolated (monomer) state in the aqueous phase and in the excimer state in the associated HEUR cores, respectively. The spectra shown here have been normalized by I_M at $\lambda = 377$ nm so as to cancel a slight fluctuation of the excitation UV intensity.

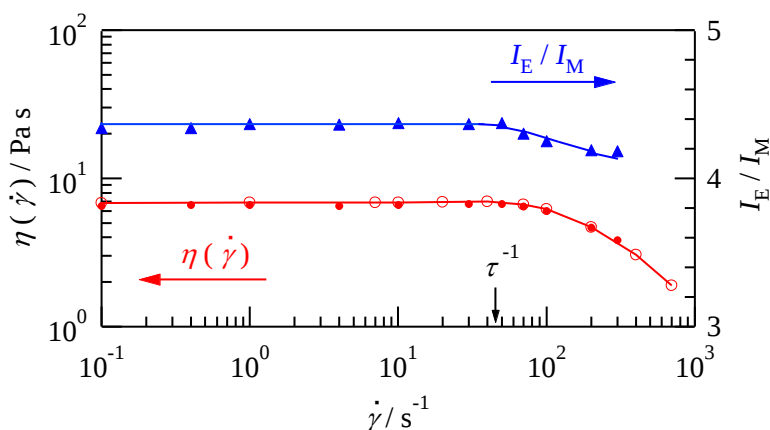


Figure 6-5. Fluorescent emission intensity I_E from excimer of associated pyrenyl groups at the HEUR chain ends in the 3.0 wt% *aq* solution under steady shear at 5 °C. This I_E is normalized by the emission intensity I_M from pyrenyl groups in the isolated monomer state in the aqueous phase and plotted against shear rate. For comparison, the shear rate dependence of the viscosity is also shown.

As noted in Figure 6-3, the HEUR solution exhibit significant decreases of both $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$, by factors of ~50% and ~75% respectively, on an increase of the shear rate well above the equilibrium relaxation frequency $1/\tau (= 45 \text{ s}^{-1})$ determined from the linear viscoelastic data shown in Figure 6-1). This thinning behavior is associated with just a slight decrease (by a factor of ~4 %) of the $I_E(\dot{\gamma})/I_M(\dot{\gamma})$ ratio (cf. Figure 6-5). This result is quite informative for specifying the thinning mechanism, as discussed below.

At equilibrium, the Py groups are dynamically associating in/dissociating from the HEUR cores, thereby allowing the thermal reorganization of the HEUR network that results in the single Maxwellian terminal relaxation in the linear viscoelastic regime. This association/dissociation balance hardly changes even under fast flow at $\dot{\gamma} = 6/\tau$, as suggested from the $I_E(\dot{\gamma})/I_M(\dot{\gamma})$ data. Thus, the significant thinning seen at those $\dot{\gamma}$ is accompanied by an almost negligible change in the HEUR core structure (as reflected in the very slight shift of the association/dissociation balance of the Py groups to the dissociated state). From this result, the thinning is quite possibly attributed to flow-induced disruption of the network connectivity through conversion of the super-bridges into super-loops, both having the same core structure. This result lends experimental support to the conventional argument for the thinning mechanism.

Finally, it should be noted that HEUR chains having Bu-Py groups at the ends examined in this chapter exhibit negligibly thickening of $\eta(\dot{\gamma})$. This behavior is in contrast to the significant thickening observed for HEUR chains having hexadecyl (HD) groups at the ends (cf. Chapters 3 and 5). This difference may be attributed to a difference of the number n of the end groups per

HEUR core: n has been reported to be ~ 22 and ~ 6 , respectively, for the HEUR chains having the HD and Bu-Py groups at the chain ends. The superbridges sustaining the high viscosity in the thickening regime can be easily disrupted (converted to the loops) for small n , thereby possibly resulting in the lack of thickening for the HEUR chains having the Bu-Py groups.

4. Conclusion

For the 3.0 wt% aqueous solution of HEUR chains having butyl-pyrenyl groups at the ends, linear and nonlinear viscoelastic behavior was examined. The HEUR chains formed a transient network sustained by cores of associating end groups. The single-Maxwellian terminal relaxation reflecting the thermal reorganization of this network was observed in the linear viscoelastic regime. Under steady shear flow, the HEUR solution exhibited thinning of both viscosity $\eta(\dot{\gamma})$ and first normal stress coefficient $\Psi_1(\dot{\gamma})$ at shear rates $\dot{\gamma}$ above the equilibrium relaxation frequency $1/\tau$. Fluorescence experiment suggested that the HEUR core structure is hardly affected even under fast shear in the thinning regime. Thus, the thinning of $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ is most likely due to flow-induced disruption of the network connectivity through conversion of the superbridges into superloops, both having the same core structure.

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Chapter 7: Summary and Conclusion

In this thesis, the rheological properties of HEUR aqueous solutions were systematically studied. Following introductory parts in Chapters 1 and 2, the shear thickening and thinning behavior of HEUR aqueous solutions and the concentration dependence of rheological properties of HEUR aqueous solutions were investigated. To explain experimental results, new theoretical models were proposed, instead of the conventional transient network type models. The main results are summarized below.

In Chapter 3, the shear thickening and thinning behavior of the 1wt% HEUR aqueous solution was studied. The shear viscosity $\eta(\dot{\gamma})$ exhibited the shear thickening (at the shear rate near the inverse relaxation time $1/\tau$) followed by the shear thinning, whereas the first normal stress coefficient $\Psi_1(\dot{\gamma})$ exhibited only the shear thinning. Such an experimental result cannot be reasonably explained by the conventional transient network type models that incorporate the FENE effects and/or the shear-induced increase of the active chain density. The measured viscosity and first normal stress growth and decay functions were also inconsistent with the predictions of the conventional models. To explain those experimental results, a new transient network type model that incorporates the anisotropic reassociation effect was proposed. The anisotropic reassociation process was considered as an essential mechanism that reproduces the shear thickening behavior, instead of the FENE and active chain density increase effects.

The anisotropic reassociation process was expected to be related to the network structure in the HEUR aqueous solution. The network structures can depend on the HEUR concentration. Thus, in

Chapters 4 and 5, the concentration dependence of the linear and nonlinear rheological properties of the HEUR aqueous solutions was investigated. The relaxation time τ and the characteristic modulus G_0 exhibited the different concentration dependence at the high and low concentrations. On the basis of this experimental result, two different network types were proposed. At the high concentrations, the bridge chains form dense networks, while at low concentrations, the superbridge chains form sparse networks. The nonlinear rheological properties were also different at high and low concentrations. The shear thickening behavior (of the viscosity) was observed only at low concentrations (namely, only for the sparse networks). To explain this concentration dependence, transient network models incorporating the effects of the functionality of the network and the spatial distribution of micellar cores were constructed. Thus constructed dense and sparse network models reproduced the linear and nonlinear rheological properties qualitatively.

The shear thinning behavior was observed both the shear viscosity and the first normal stress difference, at all the examined concentrations. The particle imaging velocimetry measurements showed that the thinning is associated with the shear banding if the shear rate is sufficiently high. To examine the shear thinning mechanism in the moderate shear rate region, the fluorescent measurements under shear flow were performed in Chapter 6. The measurements showed that the structure of the micellar core in the HEUR aqueous solution was hardly affected by the shear flow. This result suggested that the shear thinning at moderate shear rates was caused by the decrease of the active chain density (i.e., disruption of the network connectivity) occurring through conversion of superbridges into superloops.

List of Publications

1. “Nonlinear Rheology of Telechelic Associative Polymer Networks: Shear Thickening and Thinning Behavior of Hydrophobically Modified Ethoxylated Urethane (HEUR) in Aqueous Solution

Suzuki, S.; Uneyama, T.; Inoue, T.; Watanabe, H.

Macromolecules **2012**, 45, 888-898.

2. Concentration Dependence of Rheological Properties of Telechelic Associative Polymer Solutions

Uneyama, T.; Suzuki, S.; Watanabe, H.

Phys. Rev. E **2012**, 86, 031802.

3. Concentration Dependence of Nonlinear Rheological Properties of Hydrophobically Modified Ethoxylated Urethane Aqueous solutions

Suzuki, S.; Uneyama, T.; Watanabe, H.

Macromolecules **2013**, 46, 3497-3504.

4. Rheology of Aqueous Solution of Hydrophobically Modified Ethoxylated Urethane (HEUR) with Fluorescent Probes at Chain Ends: Thinning Mechanism

Suzuki, S.; Uneyama, T.; Inoue, T.; Watanabe, H.

Nihon Reoroji Gakkaishi (J. Soc. Rheol. Jap) **2012**, 40, 31-36.

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